

The Effect of One Salt upon the Hydrating Power of Another Salt
Present in the Same
Solution

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

CHARLES M. A. STINE.

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This investigation was undertaken at the suggestion of Professor Jones, and was carried out under his supervision.

The Effect of One Salt on the Hydrating Power of Another Salt Present in the Same Solution.

Six independent lines of evidence, all pointing to the existence of hydrates in aqueous solutions, having been established, it seemed desirable to attempt to determine, if possible, the effect of one salt with hydrating power upon the hydrates formed by a second salt in the same solution; also the effect of a salt with very small hydrating power on the hydrates formed by another salt. When both salts possess the power of forming hydrates in single solution, the amounts of water taken up by the salts at the same concentrations may be the same, or may vary within wide limits. We proposed to study binary mixtures in which both conditions are illustrated.

Since we desired to calculate, as accurately as possible, the approximate composition of the hydrates formed in the mixtures, it was necessary to obtain data for the freezing points, conductivities, and number of grams of solvent in a liter of solution of the various salts employed. In order that we might have the data for the exact normalities of the solutions which we mixed, it seemed advisable to make the necessary

measurements in the single solutions, rather than to attempt to interpolate from data previously obtained.

CONDUCTIVITY CALCULATIONS.

It is well known that when two or more electrolytes are present in the same solution, the conductivity of this solution is not, in general, equal to the sum of the conductivities which these electrolytes have in separate solutions of the same normality as that which these salts may be assumed to have in the mixture; but that the conductivity of the mixture is generally less than this sum. If the solutions are isohydric,¹ that is, if the component solutions possess a common ion in equal concentration, then the simplest condition exists between the conductivities of the single solutions and that of the mixture. This latter condition exists when

$$\frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2},$$

in which α_1 is the dissociation of one of the electrolytes at the dilution v_1 , and α_2 is the dissociation of the other electrolyte at the dilution v_2 . Such solutions can be mixed in any proportion without altering their dissociation, and, hence, the conductivity of the mixture is the mean of the conductivities of the component solutions and can, therefore, be calculated according to the equation

$$k = \frac{k_1P + k_2P'}{P + P'},$$

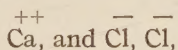
in which k_1 and k_2 are the conductivities, and P and P' the proportions of the component solutions.

Unfortunately, we have to deal with no such simple relations as these in the mixtures with which we worked.

In our work, the viscosity of the mixtures differs considerably, in many cases, from that of the single solutions assumed to have the same normality. This would involve changes in friction in the movement of the ions. Also, the amount of water combined as hydrate, *i. e.*, the dimensions of the atmos-

¹ Arrhenius: Wied. Ann., **30**, 51 (1887); Z. physik. Chem., **2**, 284 (1888).

phere about the ion, continually changed from one normality to another. This involved a varying degree of freedom of movement of the ions. Again, the variation in the number of particles present, ions and molecules, must involve continual variation in the amount of friction between the ions. As a comparatively short, and at the same time sufficiently accurate, method, we have adopted the following in apportioning the diminution in conductivity to the constituent salts: Since we have dealt in every case with mixtures in which the two electrolytes have a common ion, we have based the method on the number of this common ion yielded by the constituent salts in separate solutions at the same normality. By the same normality, we mean that if equal volumes of two solutions are mixed, and any diminution in volume which may take place upon mixing is compensated for by the addition of pure solvent, then the normality of each solution in the mixture may be assumed to be exactly half of that of the constituent solutions. If suppression of the ionization is dependent upon the common ion, then it will be inversely as the number of this common ion furnished by each of the salts in a mixture. This number was obtained thus: The figure representing the normality of the individual solutions, multiplied by the value of α for the solution at the normality in question, would give the gram atomic weight of the common ion. Suppose the case to be one where a solution of potassium chloride has been added to an equal volume of a solution of calcium chloride. It being assumed that calcium chloride dissociates into



the figure representing the gram atomic weight of the common ion would have to be doubled for a ternary electrolyte, such as calcium chloride. Since two chlorine ions are required to re-form a molecule of calcium chloride, the figure expressing the number of chlorine ions driven back, in the case of calcium chloride, must be divided by two, in order to get the relative number of molecules of calcium chloride re-formed.

Let us take the values of Λ_{∞} as expressing the molecular conductivity of the completely dissociated molecules of the various salts. If the figures for the relative numbers of molecules of the two salts re-formed be multiplied by the proper value of Λ_{∞} , we shall then have the relative losses in conductivity. From this the absolute losses are readily obtained. An example may suffice to make this clear: Take the case of the mixture of equal volumes of a solution of 1.8 N calcium chloride and of 1.7 N potassium chloride. The resulting solution, any diminution of volume having been compensated for, will consist of 0.9 N calcium chloride and 0.85 N potassium chloride. The dissociation of a 0.9 N solution of the specimen of calcium chloride employed was found, by conductivity measurements, to be 53.2 per cent, of 0.85 N potassium chloride, 83.2 per cent. Doubling the value of α in the case of calcium chloride and multiplying by the normality, we get 0.9576. Similarly, for potassium chloride, 0.7068. These represent the relative numbers of chlorine ions which would be furnished by each salt in the mixture if no suppression of the ionization took place upon mixing. That is, if driving back occurs, according to the law of mass action, 707 chlorine ions should be driven back to re-form calcium chloride to 958 for potassium chloride. But since it requires two ions of chlorine to re-form each molecule of calcium chloride, only 354 molecules of calcium chloride will be re-formed to every 958 molecules of potassium chloride. Multiplying these values by Λ_{∞} for calcium chloride and potassium chloride, respectively, we get 5222, approximately, for calcium chloride and 7695 for potassium chloride. These values represent the relative losses in conductivity upon mixing. From this the decrease in conductivity can be apportioned between the two salts.

All conductivity measurements are given as specific conductivities in the mixtures. The units employed are reciprocal centimeter ohms. For purposes of comparison with the previous work upon the "hydrate theory" our units may be transformed by dividing Λ_v by 1.069.

The approximate composition of the hydrates in the *single*

solutions was calculated by the method previously employed by Jones and his coworkers.

EXPERIMENTAL WORK.

Freezing Point.—The more concentrated solutions were frozen by means of a mixture of solid carbon dioxide and alcohol, the freezing temperature being determined by means of alcohol thermometers. These temperatures could not be measured more closely than $0^{\circ}.5$. For the more dilute solutions freezing mixtures of ice and sodium chloride, or ice and crystallized calcium chloride, were employed. The temperature was read by means of Beckmann thermometers, covering ranges of 6° , 12° , and 25° , respectively. When the more concentrated solutions were frozen, they were removed from the bath of solid carbon dioxide and alcohol as soon as ice began to separate, in order that they might not be surrounded by the very cold freezing mixture while temperature equilibrium was being established. The necessary correction for the separation of ice and consequent increase in concentration was introduced in every instance. The separation of some of the dissolved substance was readily ascertained by the grit or sandlike character of the solid that separated, which was easily detected. Since it was found that, for the volume of liquid employed in the freezing point tube (about twenty-five cubic centimeters), a freezing point determination made with a large undercooling and, consequently, a copious separation of ice gave a slightly different result from one where the undercooling was less, care was taken, in the freezing point determinations of both the pure solvent and the solutions, to keep the undercooling nearly the same throughout—about a degree. This necessitated innoculating the solution, in nearly every case, with an exceedingly minute particle of the solid phase of the solvent.

CONDUCTIVITY.

Conductivities were measured by the method of Kohlrausch.

The resistance coils, manufactured by Leeds & Co., were

tested and found in no case to involve a greater error than 0.04 per cent.

The dilute solutions were measured in conductivity cells of the form employed by Jones and Bingham,¹ the tubes carrying the platinum electrodes being sealed into both the upper and lower walls of the stopper. For the more concentrated solutions, cells of the type used by Jones and Getman² were employed. The electrodes were treated in the usual manner (coated with platinum black, etc.), in order to obtain a sharper tone minimum or point of silence in the readings.

The cells for the more dilute solutions were standardized by determining the cell constant by means of N/50 potassium chloride. The value $k = 0.0015133$ was taken as the conductivity of N/50 potassium chloride. For the more concentrated solutions, the cell constants were determined with a N/2 solution of potassium chloride, for which $k = 0.03365$ at 0°.³ The potassium chloride employed in determining cell constants was recrystallized five times, the last two times from conductivity water, and was free from all appreciable impurities. The cell constants were frequently redetermined, but very little change in them was noted from time to time. The cells were filled with distilled water when not in use, and were always carefully cleansed, dried, and rinsed with the new solution when a change in solutions was made. All conductivities were measured at 0°. The temperature of the zero bath was always within a tenth of a degree of 0°, as determined by an accurately standardized thermometer. All conductivity measurements are the average of four readings with different resistances in circuit.

The water used in this work was purified as in former work.

It is well known that the conductivity method is not an accurate measure of dissociation in concentrated solutions. Especially is this the case at the concentrations with which we dealt, since the values of Λ_{∞} , which we used in our mixtures, were determined for each salt by diluting the single

¹ THIS JOURNAL, **34**, 481 (1905).

² Z. physik. Chem., **46**, 254 (1903).

³ These values are calculated from the results of Jones and West. See THIS JOURNAL, **34**, 381 (1905).

solution to a maximum value of Λ_v . This is, obviously, a source of additional error, for the conductivity of the ions resulting from a completely dissociated molecule in a very dilute solution must be different from the conductivity of those ions in a more concentrated solution. In the more dilute solution a larger atmosphere of the solvent is attached to the ions, and this must be dragged along by them. There is present a much smaller number of particles of salt (ions or molecules) in the dilute than in the more concentrated solution. Consequently, the friction between the ions in their movements must be different. The viscosity of the solutions in which Λ_∞ can be determined is very much less than the viscosity of the solutions at the concentrations employed. These are all important factors which affect the conductivity of any dissolved substance. The method is, however, an approximate one for measuring such dissociations, and is the best available at present. All that can be said is that it probably gives values of the right order of magnitude.

CALCIUM CHLORIDE.

A strong solution of calcium chloride was prepared and standardized. All solutions were made by diluting the calculated amount of the original solution to the required volume.

Table I.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>m.</i>	Δ .	Δ/m .
0.3	1°.517	5.056	1.4	10°.05	7.18
0.5	2°.672	5.344	1.55	11°.58	7.47
0.6	3°.270	5.450	1.755	14°.33	8.16
0.7	4°.065	5.807	1.88	14°.69	8.16
0.9	5°.422	6.024	2.2	21°.07	9.58
1.0	6°.410	6.310	2.7	30°.25	11.20
1.1	7°.080	6.436	3.1	39°.5	12.74
1.35	9°.362	6.934	3.5106	49°.5?	14.10?

In this table, as elsewhere where they occur, *m* is the concentration in terms of gram molecules per liter; Δ , the observed freezing point lowering, corrected for the separation of ice; and Δ/m , the molecular lowering of the freezing point.

Table II.—Conductivity Measurements.

$\Lambda_{\infty} 0^{\circ} = 147.52.^1$				
$m.$	$V.$	$k.$	$\Lambda_v.$	$\alpha.$
0.3	3.333	0.028044	93.5	0.634
0.5	2.000	0.043801	87.6	0.594
0.6	1.6666	0.050268	83.8	0.568
0.7	1.4285	0.057555	82.2	0.557
0.9	1.1111	0.070601	78.4	0.532
1.0	1.000	0.075540	75.5	0.512
1.1	0.909	0.081573	74.1	0.502
1.35	0.7407	0.092860	68.8	0.466
1.4	0.7143	0.09396	67.1	0.455
1.55	0.6453	0.099184	64.0	0.434
1.755	0.5698	0.10723	61.1	0.414
1.8	0.5555	0.107267	59.8	0.405
2.2	0.4545	0.115876	52.7	0.357
2.7	0.3704	0.7757	43.6	0.296
3.1	0.3226	0.11410	36.8	0.250
3.5106	0.2849	0.10710	30.5	0.207

In this table, as elsewhere throughout this paper, m is the concentration, in terms of gram molecules per liter; V is the number of liters that contain a gram molecule of the dissolved substance; k is the specific conductivity, and is equal to

$$\frac{0.001069\mu_v}{v},$$

Λ_v is the molecular conductivity at 0° , and is equal to $1000 \times V \times k$; α is the percentage of dissociation, and is equal to $\Lambda_v/\Lambda_{\infty}$.

Table III.—Weight-Normal Corrections, or Number of Grams of Solvent in 1000 Cubic Centimeters of Solution.

$m.$	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. per cent.
0.3	51.270	1.665	49.605	0.8
0.5	52.2608	2.775	49.4858	1.0
0.6	52.7437	3.33	49.4137	1.2
0.7	53.1162	3.885	49.2312	1.5
0.9	53.9816	4.995	48.9866	2.0
1.0	54.326	5.55	48.776	2.4

¹ Calculated from the value given by Jones and Bassett: *THIS JOURNAL*, 32, 547 (1905).

Table III—(Continued).

m .	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
1.1	54.772	6.105	48.667	2.7
1.35	55.9435	7.4925	48.451	3.1
1.4	56.115	7.770	48.345	3.3
1.55	56.6562	8.6025	48.0537	3.9
1.755	57.7040	9.7402	47.9638	4.1
1.8	28.900	4.995	23.905	4.4
2.2	29.650	6.105	23.545	5.8
2.7	30.682	7.492	23.190	7.2
3.1	31.461	8.602	22.859	8.6
3.5106	32.187	9.720	22.467	10.1

In these tables of weight-normal corrections, m has the usual significance; $W_{Sol.}$ is the weight of twenty-five or of fifty cubic centimeters of the solution; $W_{Salt.}$ is the weight of salt contained in this volume of the solution; W_{H_2O} is the weight of water in this volume of solution, equal to $W_{Sol.} - W_{Salt.}$; "Correction, per cent." is the percentage of correction to be applied in order to refer measurements to a thousand grams of solvent. These are not specific gravity measurements made in pycnometers, and we therefore give the correction percentage only to the first decimal.

In the following tables, as in all other tables of the hydrates formed in the single solutions, m has the usual significance; α is the percentage of dissociation; L is the theoretical molecular lowering of the freezing point referred to a thousand grams of the solvent; Δ/m , the molecular lowering found experimentally; L' , the molecular lowering; M , the number of gram molecules of water in combination, both being referred to a thousand grams of solvent—

$$M = \frac{1000 - \left[\frac{L}{L'} \times 1000 \right]}{18}.$$

H is the number of molecules of water in combination with one molecule of the salt, at the concentration in question, if a liter of the solution at that concentration contained a thousand grams of water. It equals M/m .

Table IV.—Hydrates.

$m.$	$\alpha.$	$L.$	$\Delta/m.$	$L'.$	$M.$	$H.$
0.3	0.634	4.22	5.06	5.02	8.8	29.4
0.5	0.594	4.09	5.34	5.29	12.6	25.2
0.6	0.568	3.97	5.45	5.39	14.6	24.3
0.7	0.557	3.93	5.81	5.72	17.4	24.8
0.9	0.532	3.84	6.02	5.90	19.4	21.6
1.0	0.512	3.76	6.31	6.16	21.6	21.6
1.1	0.502	3.73	6.44	6.26	22.4	20.4
1.35	0.466	3.59	6.93	6.72	25.9	19.2
1.4	0.455	3.55	7.18	6.94	27.2	19.4
1.55	0.434	3.47	7.47	7.18	28.7	18.5
1.755	0.414	3.40	8.16	7.83	31.4	17.9
1.8	0.405	3.37	8.16	7.80	31.6	17.5
2.2	0.357	3.19	9.58	9.03	35.9	16.3
2.7	0.296	2.96	11.20	10.39	39.7	14.7
3.1	0.250	2.79	12.74	11.65	43.6	14.1
3.5106	0.207	2.63	14.10	12.68	46.5	13.2

Since we wished to investigate the effect of the presence of a salt with little hydrating power upon a salt with considerable hydrating power, potassium chloride was added to calcium chloride. The data for the various solutions of potassium chloride alone are next given.

POTASSIUM CHLORIDE.

Table V.—Freezing Point Measurements.

$m.$	$\Delta.$	$\Delta/m.$	$m.$	$\Delta.$	$\Delta/m.$
0.45	1° 52	3.35	1.2972	4° 48	3.45
0.65	2° 24	3.45	1.3	4° 49	3.46
0.85	2° 91	3.43	1.7	5° 93	3.49
0.90	3° 08	3.42	2.1	7° 43	3.54
1.05	3° 58	3.41	2.5945	9° 29	3.58

Table VI.—Conductivity Measurements.

$$\Lambda_{\infty} 0^{\circ} = 80.33.^1$$

$m.$	$V.$	$k.$	$\Delta v.$	$\alpha.$
0.45	2.222	0.030332	67.4	0.839
0.65	1.538	0.043608	67.1	0.835
0.85	1.1765	0.056804	66.8	0.832
0.90	1.1111	0.058717	65.2	0.812

¹ Calculated from the value given by Jones and West: THIS JOURNAL, 34, 381 (1905).

Table VI—(Continued).

<i>m.</i>	<i>V.</i>	<i>k.</i>	$\Delta v.$	$\alpha.$
1.05	0.9523	0.068969	65.7	0.818
1.2972	0.7709	0.083948	64.7	0.805
1.3	0.7792	0.084118	64.7	0.805
1.7	0.5882	0.109202	64.2	0.800
2.1	0.4762	0.133785	63.7	0.793
2.5945	0.3854	0.163207	62.8	0.782

Table VII.—Weight-Normal Corrections.

<i>m.</i>	<i>W_{Sol.}</i>	<i>W_{Salt.}</i>	<i>W_{H₂O.}</i>	Correction. per cent.
0.45	8.0042	0.26353	7.74067	1.4
0.65	8.0735	0.38066	7.69284	2.0
0.85	8.1443	0.49654	7.64766	2.6
0.90	25.9936	1.6785	24.3151	2.7
1.05	8.2169	0.61492	7.60198	3.2
1.3	26.5127	2.4245	24.0882	3.7
1.7	26.928	3.1705	23.7575	5.0
2.1	27.4457	3.9165	23.5292	5.9
2.5945	28.0254	4.8385	23.1869	7.3

Table VIII.—Hydrates.

<i>m.</i>	$\alpha.$	<i>L.</i>	$\Delta/m.$	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.45	0.839	3.42	3.35	3.30		
0.65	0.835	3.41	3.45	3.38		
0.85	0.832	3.41	3.43	3.34		
0.90	0.812	3.37	3.42	3.32		
1.05	0.818	3.38	3.41	3.40		
1.2972	0.805	3.36	3.45	3.33		
1.3	0.805	3.36	3.46	3.33		
1.7	0.800	3.35	3.49	3.31		
2.1	0.793	3.34	3.54	3.33		
2.5945	0.782	3.32	3.58	3.32		

There is evidently no hydrating power.

MIXTURE OF CALCIUM CHLORIDE AND POTASSIUM CHLORIDE.

Table IX.—Freezing Point Measurements.

<i>m.</i>	<i>P.</i>	$\Delta.$	<i>m.</i>	<i>P.</i>	$\Delta.$
1.0 CaCl ₂	I		2.7 CaCl ₂	I	
0.9 KCl	I	4°.413	2.5945 KCl	I	15°.00
1.4 CaCl ₂	I		3.1 CaCl ₂	I	
1.3 KCl	I	6°.625	2.5945 KCl	I	16°.50
1.8 CaCl ₂	I		3.5106 CaCl ₂	I	
1.7 KCl	I	9°.17	2.5945 KCl	I	18°.0
2.2 CaCl ₂	I				
2.1 KCl	I	12°.01			

Table X.—Conductivity Measurements.

<i>m.</i>	<i>P.</i>	<i>m_c.</i>	<i>V_c.</i>	<i>k_u.</i>	<i>k.</i>	<i>D.</i>	<i>k_c.</i>	$\Delta v.$	$\alpha.$
1.0 CaCl ₂	I	0.5	2.0000	0.069977	0.043801	0.004158	0.048890	84.6	0.573
0.9 KCl	I	0.45	2.2220		0.030332		0.027687	61.5	0.766
1.4 CaCl ₂	I	0.7	1.4285		0.057555		0.054653	78.1	0.529
1.3 KCl	I	0.65	1.5380	0.093713	0.043608	0.00745	0.039060	60.0	0.748
1.8 CaCl ₂	I	0.9	1.1111		0.070601	0.013309	0.065221	72.5	0.491
1.7 KCl	I	0.85	1.1765	0.114096	0.056804		0.048875	56.5	0.716
2.2 CaCl ₂	I	1.1	0.9090		0.081573		0.073353	66.7	0.452
2.1 KCl	I	1.05	0.9523	0.13081	0.068969	0.01973	0.057459	54.7	0.681
2.7 CaCl ₂	I	1.35	0.7407	0.14805	0.092860	0.02876	0.080410	59.6	0.404
2.5945 KCl	I	1.2972	0.7709		0.083948		0.067650	52.2	0.649
3.1 CaCl ₂	I	1.55	0.6451	0.15081	0.099184		0.057794	55.4	0.375
2.5945 KCl	I	1.2972	0.7709		0.083948	0.03232	0.065018	50.1	0.624
3.5106 CaCl ₂	I	1.755	0.5698	0.15239	0.107230		0.091830	52.3	0.355
2.5945 KCl	I	1.2972	0.7709		0.083948	0.03879	0.060560	46.7	0.581

In Table IX. the column headed P indicates parts by volume of each solution which were mixed; m is the normality of the solutions before mixing. In order that each solution should have exactly one-half the normality after mixing which it had before, the volume of the mixture was brought to exactly twice the volume by the addition of either of the constituent solutions.

In Table X. m is the normality of the solutions mixed. P is the parts by volume of each solution which were mixed. When equal volumes are mixed the resulting normality of each solution is exactly one-half of that of the solutions before mixing. This is given under m_c . V_c is the number of liters of solution that will contain a gram molecular weight of the salt, based on m_c . k_u is the specific conductivity of the mixture. This would be the sum of the conductivities of the component solutions if no suppression of the ionization occurred. k gives the conductivities of the single solutions of each salt at the normality acquired upon mixing. In each case the sum of these two, minus the conductivity of the mixture, k_u , gives the decrease in conductivity due to the driving back of the dissociation of the salts in question. This is given under D . This loss in conductivity is then apportioned to each electrolyte by the method already described, and the resulting conductivities are given under k_c . From this, Λ_v and α are obtained.

Table XI.—Weight-Normal Corrections.

m .	P .	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
1.0 $CaCl_2$	I	26.7448	2.22637	24.51843	1.9
0.9 KCl	I				
1.4 $CaCl_2$	I	27.3662	3.1542	22.2120	3.2
1.3 KCl	I				
1.8 $CaCl_2$	I	28.0354	4.0827	23.9527	4.2
1.7 KCl	I				
2.2 $CaCl_2$	I	28.6177	5.0102	23.6075	5.6
2.1 KCl	I				
2.7 $CaCl_2$	I	29.422	6.1655	23.2565	6.9
2.59 KCl	I				
3.1 $CaCl_2$	I	29.8247	6.7205	23.1042	7.6
2.59 KCl	I				
3.51 $CaCl_2$	I	30.2118	7.2793	22.9235	8.3
2.59 KCl	I				

Proceeding upon the tentative hypothesis that the calcium chloride forms the same hydrates in the presence of a salt with no hydrating power that it forms in separate solution, the values in Tables XII. and XIII. were calculated.

Table XII.—Calcium Chloride in the Mixture.

<i>m.</i>	<i>P.</i>	<i>mc.</i>	α .	<i>L.</i>	<i>I.</i>
1.0 CaCl ₂	I				
0.9 KCl	I	0.5	0.573	3.992	2.034
1.4 CaCl ₂	I				
1.3 KCl	I	0.7	0.529	3.829	2.769
1.8 CaCl ₂	I				
1.7 KCl	I	0.9	0.491	3.687	3.464
2.2 CaCl ₂	I				
2.1 KCl	I	1.1	0.452	3.541	4.126
2.7 CaCl ₂	I				
2.59 KCl	I	1.35	0.404	3.362	4.880
3.1 CaCl ₂	I				
2.59 KCl	I	1.55	0.375	3.256	5.462
3.51 CaCl ₂	I				
2.59 KCl	I	1.7553	0.355	3.179	6.084

α is the dissociation of the calcium chloride in the mixture. *L* is the freezing point lowering calculated from the formula $(1.86 \times 2\alpha) + 1.86$. *I* is the freezing point lowering, corrected to one thousand grams of solvent, which the salt would give if there were no hydration.

Table XIII.

<i>m.</i>	<i>P.</i>	<i>mc.</i>	α .	Δ .	<i>WH₂O.</i>	Correction, per cent.	<i>I.</i>
1.0 CaCl ₂	I						
0.9 KCl	I	0.45	0.766	1.478	753.7	24.6	1.961
1.4 CaCl ₂	I						
1.3 KCl	I	0.65	0.748	2.113	655.9	34.4	3.222
1.8 CaCl ₂	I						
1.7 KCl	I	0.85	0.716	2.712	608.2	39.2	4.454
2.2 CaCl ₂	I						
2.1 KCl	I	1.05	0.681	3.283	538.5	46.2	6.097
2.7 CaCl ₂	I						
2.59 KCl	I	1.2972	0.649	3.068	464.7	53.5	8.564
3.1 CaCl ₂	I						
2.59 KCl	I	1.2972	0.624	3.021	408.0	59.2	9.605
3.51 CaCl ₂	I						
2.59 KCl	I	1.2972	0.581	2.941	340.5	66.0	11.20

α is the dissociation of the potassium chloride in the mixture; Δ is the freezing point lowering deduced from $[(1.86 \times \alpha) + 1.86]m_c$; W_{H_2O} is the weight of water acting as solvent towards the potassium chloride, deduced from $L : L :: X : 1000$, which gives the amount of water taken up by the calcium chloride in the formation of hydrates when it alone is present in solution, and from the weight-normal correction for the mixture; I is the ideal lowering which the potassium chloride would give if the calcium chloride formed the same hydrates in the mixture that it forms when alone in solution.

Table XIV.—Comparison of Lowerings due to Hydration in Separate Solution of Calcium Chloride and in the Mixture.

$m.$	$m_c.$	$\Delta_c.$	$I_c.$	$\text{Diff}_c.$	$\Delta.$	$I.$	Diff.
1.0 CaCl_2	0.5	4.413	3.995	$0^\circ.418$	2.672	2.066	$0^\circ.606$
0.9 KCl							
1.4 CaCl_2	0.7	6.625	5.991	$0^\circ.634$	4.004	2.750	$1^\circ.25$
1.3 KCl							
1.8 CaCl_2	0.9	9.170	7.918	$1^\circ.252$	5.314	3.455	$1^\circ.859$
1.7 KCl							
2.2 CaCl_2	1.1	12.01	10.223	$1^\circ.782$	6.896	4.100	$2^\circ.799$
2.1 KCl							
2.7 CaCl_2	1.35	15.0	13.442	$1^\circ.558$	9.072	4.851	$4^\circ.221$
2.59 KCl							
3.1 CaCl_2	1.55	16.5	15.067	$1^\circ.433$	11.13	5.385	$5^\circ.745$
2.59 KCl							
3.51 CaCl_2	1.7553	18.0	17.288	$0^\circ.712$	14.10	5.970	$8^\circ.130$
2.59 KCl							

($P = 1$ in every case.)

Δ_c is the lowering found experimentally for the mixture. I_c is the sum of I in Tables XII. and XIII. $\text{Diff}_c = \Delta_c - I_c =$ lowering due to hydration. Δ is the lowering found experimentally for calcium chloride, corrected to one thousand grams of solvent. I is the lowering the calcium chloride should have given in 1000 grams of solvent, if there were no hydration. Evidently, $\text{Diff}_c.$ and Diff. should be identical if there were no change in hydration. Such is not the case. Consequently, the basis assumed for the calculation of I for potassium chloride in the mixture is incorrect, since it depends upon a knowledge of the amount of water eliminated from the sphere of action as solvent by the hydration of the cal-

cium chloride. It, therefore, becomes necessary to derive a formula for the calculation of the hydration of the calcium chloride in the mixture.

FORMULA FOR CALCULATING LOWERING DUE TO HYDRATION, IN A
BINARY MIXTURE OF ELECTROLYTES, WHERE ONE SALT
HAS NO HYDRATING POWER.

Let X degrees equal lowering due to hydration of the salt with hydrating power in the mixture.

I = theoretical lowering which the salt with hydrating power should give in the mixture in question, at the corrected dissociation, if there were no hydration.

V = number of liters that contain a gram molecule of the salt with hydrating power, at the normality it has in the mixture.

Then,

$$(X + I)v = \Delta/m.$$

s = correction to 1000 grams of solvent, necessary in the mixture.

$$(X + I)v - (X + I)vs = L'.$$

X' = amount of water acting as solvent towards the salt with *no* hydrating power.

$$L : L' :: X' : 1000.$$

$L = (1.86 \times 2\alpha) + 1.86$, in a ternary electrolyte, where α represents the corrected dissociation of the salt with hydrating power *in the mixture*.

$$\frac{(1.86 \times 2\alpha) + 1.86}{(X + I)v - (X + I)vs} \cdot 1000 = X'.$$

But taking into account the weight-normal correction also, in the mixture in question, the above becomes

$$\left[\frac{(1.86 \times 2\alpha) + 1.86}{(X + I)v - (X + I)vs} \cdot 1000 \right] - 10 S =$$

amount of water actually acting as solvent towards the salt with *no* hydrating power. Putting this into the form of a percentage correction,

$$\frac{(1.86 \times 2\alpha) + 1.86}{(X + I)v - (X + I)vs} - \frac{S}{100} =$$

the per cent by which *I* for the salt with little, or no, hydrating power must be divided.

Let α' = the corrected dissociation in the mixture of the salt with no hydrating power,

$$[(1.86 \times \alpha') + 1.86]m =$$

lowering it would give in 1000 grams of solvent, if it is a binary electrolyte. *m* is the normality of the salt with no hydrating power.

Then,

$$\frac{\frac{1.86m(\alpha' + 1)}{1.86(2\alpha + 1)} - \frac{S}{100}}{(X + I)(v - vs)} + X + I =$$

lowering found experimentally for the mixture. From this expression the value of *X* may be derived.

By means of this formula the value of *X* has been calculated for the various concentrations employed in the mixture of calcium chloride and potassium chloride, and the results are given in Table XV. The significance of the abbreviations has already been given in connection with the preceding tables.

In order to compare the hydrates formed by calcium chloride in separate solution with those which it forms in the mixture with potassium chloride, the values of *M* are plotted against the concentrations as abscissas in Fig. I.

It is seen that while the value of *M* increases with increase in concentration, in general, in the mixture as in separate solution, *M* is less in the mixture than in separate solution of calcium chloride. This is just what we should expect, since there is less water present as solvent in the mixture of calcium chloride and potassium chloride, at any given concentration of the calcium chloride, than there is at the same

Table XV.—Hydration of CaCl_2 in Mixture.

<i>m.</i>	<i>P.</i>	<i>M_c.</i>	<i>α.</i>	<i>L.</i>	<i>I.</i>	<i>X.</i>	<i>Δ/m.</i>	<i>L'.</i>	<i>M.</i>	<i>H.</i>
1.0 CaCl_2	I	0.5	0.573	3.92	2.034	0.456	4.981	4.886	10.2	23.8
0.9 KCl	I									
1.4 CaCl_2	I	0.7	0.529	3.829	2.769	0.909	5.254	5.086	13.7	19.6
1.3 KCl	I									
1.8 CaCl_2	I	0.9	0.491	3.687	3.464	1.537	5.556	5.323	17.1	19.0
1.7 KCl	I									
2.2 CaCl_2	I	1.1	0.452	3.541	4.126	2.291	5.834	5.507	19.8	18.0
2.1 KCl	I									
2.7 CaCl_2	I	1.35	0.404	3.362	4.88	2.94	5.978	5.387	20.9	15.5
2.59 KCl	I									
3.1 CaCl_2	I	1.55	0.375	3.256	5.462	3.601	5.847	5.403	22.1	14.3
2.59 KCl	I									
3.51 CaCl_2	I	1.7553	0.355	3.179	6.084	4.32	5.928	5.436	23.1	13.1
2.59 KCl	I									

concentration of the single solution of calcium chloride. Now it is evident, from previous work, that while the *total number of gram molecules of water combined increases, in general, with increase in concentration, the molecular hydration decreases with increase in concentration*. That is, the amount of water with which a molecule of the calcium chloride or the resulting ions combine depends upon the number of molecules of water present to one molecule of the calcium chloride. If, now,

- I. Calcium Chloride Alone.
- II. Calcium Chloride Mixed with Potassium Chloride.

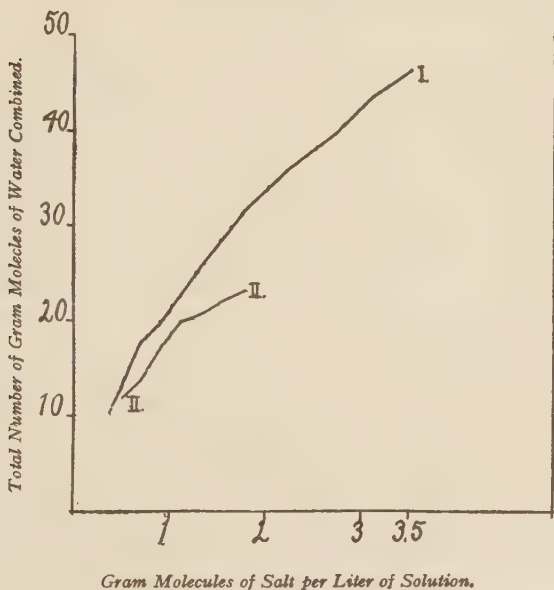


Fig. I.

instead of increasing the number of grams of salt with hydrating power present in a given solution, and thus diminishing the amount of water, we add to the calcium chloride a substance like potassium chloride and then make up to the former volume, it is evident that, there being less water present, the amount of water with which each molecule or ion of calcium chloride will combine will be diminished; that is, the value of M will be diminished.

In order to compare the difference between the amount of water present acting as solvent towards the calcium chloride in the single solution and in the mixture with the difference in the values of M in the two cases, we give in the following table, under D_{H_2O} , the difference between the number of grams of water present as solvent in the separate solution of calcium chloride and in the mixture at the respective concentrations; under D_m , the difference in the values of M for the separate solution of the calcium chloride and in the mixture at the same concentrations.

Table XVI.

m .	D_{H_2O} .	D_m .	m .	D_{H_2O} .	D_m .
0.5	9	2.4	1.35	38	4.99
0.7	17	2.8	1.55	38	6.62
0.9	22	2.34	1.7553	42	8.36
1.1	29	2.61			

These results are plotted in curves as Fig. II. For the first four concentrations the values of M decrease by the same amount, since the amount of potassium chloride added is increased as the calcium chloride is increased. Consequently, the curve for the difference in the values of M is approximately parallel to the axis of abscissas (concentration). Referring to Table XV., it will be seen that the difference between successive values of M diminishes with increase in concentration, until finally, in the mixture containing 2.7 N calcium chloride and 2.59 N potassium chloride, M has the value 20.9. The effect of the potassium chloride on the amount of water with which the calcium chloride can combine is such that, although the same amount of potassium chloride is added to the succeeding mixtures, the calcium chloride can increase its water of hydration only slightly, and by a constant difference, with increase in the concentration of the calcium chloride added. Consequently, there is increasing deviation, in Fig. I., between the curve representing the value of M for the single solution and that representing M for the mixture. In Fig. II., the difference between the values of M for calcium chloride in the separate solution and in the mixture is approximately

proportional to the difference in the amount of water present acting as solvent towards the calcium chloride in the separate solution and in the mixture. This is shown by Curve II.

- I. *Difference between Amount of Water Present in the Single Solution of Calcium Chloride and Potassium Chloride.*
 II. *Difference between Values of M for Calcium Chloride in Single Solution of Calcium Chloride and in Mixture of Calcium Chloride and Potassium Chloride.*



Fig. II.

It must be borne in mind that these results are based on the assumption that calcium chloride breaks down at once into Ca^{++} , Cl^- , Cl^- ; also, that the entire decrease in conductivity upon mixing is due to re-formation of the molecules, whereas a part of the decrease is certainly due to viscosity and friction of the ionic spheres, as already mentioned.

In order to ascertain the effect upon the hydrates formed, a pair of salts, both of which have hydrating power, was next studied.

For this purpose it was considered desirable to investigate, first, a case where both the salts employed have a large hydrating power, and where the hydrating power of the two salts in single solution is of the same order of magnitude. Calcium chloride and magnesium chloride fulfill these conditions.

CALCIUM CHLORIDE.

Table XVII.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>m.</i>	Δ .	Δ/m .
0.15	0°.74	4.93	0.85	5°.05	5.94
0.25	1°.265	5.06	1.05	6°.65	6.33
0.35	1°.801	5.15	1.25	8°.41	6.73
0.45	2°.35	5.22	1.45	10°.51	7.25
0.65	3°.55	5.62			

Table XVIII.—Conductivity Measurements.

$$\Lambda_{\infty} 0^{\circ} = 147.5.$$

<i>m.</i>	<i>V.</i>	<i>k.</i>	Λ_v .	α .
0.15	6.6666	0.014991	99.9	0.677
0.25	4.0000	0.024073	96.3	0.653
0.35	2.8571	0.032700	93.4	0.633
0.45	2.2222	0.039688	88.2	0.598
0.64	1.538	0.054236	83.4	0.565
0.83	1.1765	0.066903	78.7	0.534
1.05	0.9523	0.078244	74.5	0.505
1.25	0.8000	0.088853	71.1	0.482
1.45	0.6897	0.097385	67.2	0.455

Table XIX.—Weight-Normal Corrections.

<i>m.</i>	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Correction per cent.
0.15	25.3227	0.41625	24.90645	0.4
0.25	25.5423	0.69375	24.84855	0.6
0.35	25.8040	0.97125	24.83275	0.7
0.45	26.0110	1.24875	24.76225	1.0
0.65	26.4384	1.80375	24.63465	1.5
0.85	26.8816	2.35875	24.52285	1.9
1.05	27.2846	2.91375	24.37085	2.5
1.25	27.6792	3.46875	24.21045	3.2
1.45	28.1293	4.02375	24.10555	3.6

Table XX.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\Delta/m.$	<i>L'.</i>	<i>M.</i>	<i>H.</i>
0.15	0.677	4.38	4.93	4.91	6.0	40.2
0.25	0.653	4.29	5.06	5.03	8.2	32.8
0.35	0.633	4.22	5.15	5.11	9.7	27.8
0.45	0.598	4.08	5.22	5.17	11.7	25.9
0.65	0.565	3.96	5.62	5.53	15.7	24.3
0.85	0.534	3.85	5.94	5.83	18.9	22.3
1.05	0.505	3.74	6.33	6.18	21.9	20.9
1.25	0.482	3.65	6.73	6.50	24.3	19.5
1.45	0.455	3.55	7.25	6.99	27.3	18.8

MAGNESIUM CHLORIDE.

Table XXI.—Freezing Point Measurements.

<i>m.</i>	$\Delta.$	$\Delta/m.$	<i>m.</i>	$\Delta.$	$\Delta/m.$
0.15	0°.747	4.98	0.85	5°.404	6.36
0.25	1°.306	5.22	1.05	7°.191	6.84
0.35	1°.910	5.46	1.25	9°.236	7.39
0.45	2°.537	5.64	1.45	11°.47	7.91
0.65	3°.854	5.93			

Table XXII.—Conductivity Measurements.

<i>m.</i>	<i>V.</i>	<i>k.</i>	$\Lambda_v.$	<i>α.</i>
0.15	6.6666	0.013642	90.9	0.705
0.25	4.0000	0.021529	86.1	0.667
0.35	2.8571	0.02824	80.7	0.625
0.45	2.2222	0.036183	80.4	0.623
0.65	1.538	0.047864	73.6	0.570
0.85	1.1765	0.057606	67.8	0.525
1.05	0.9523	0.066280	63.1	0.489
1.25	0.8000	0.073499	58.8	0.456
1.45	0.6896	0.078040	53.8	0.417

Table XXIII.—Weight-Normal Corrections.

<i>m.</i>	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O.}	Correction per cent.
0.15	25.2954	0.3572	24.9382	0.2
0.25	25.5072	0.5954	24.9118	0.4
0.35	25.7066	0.8333	24.8731	0.5
0.45	25.8825	1.717	24.8108	0.8
0.65	26.2378	1.5480	24.6898	1.2
0.85	26.6460	2.0243	24.6217	1.5
1.05	27.0011	2.5006	24.5005	2.0
1.25	27.3538	2.9768	24.3770	2.5
1.45	27.7095	3.4532	24.2563	3.0

Table XXIV.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	<i>Δ/m.</i>	<i>L'.</i>	<i>M.</i>	<i>H.</i>
0.15	0.705	4.48	4.98	4.97	5.5	36.5
0.25	0.667	4.34	5.22	5.20	9.2	36.7
0.35	0.625	4.19	5.46	5.43	12.7	36.3
0.45	0.601	4.10	5.64	5.58	14.9	33.1
0.65	0.570	3.98	5.93	5.86	17.8	27.4
0.85	0.525	3.81	6.36	6.26	21.7	25.6
1.05	0.489	3.68	6.84	6.70	25.1	23.9
1.25	0.456	3.56	7.39	7.20	28.1	22.5
1.45	0.417	3.41	7.91	7.67	30.9	21.3

MIXTURE OF CALCIUM CHLORIDE AND MAGNESIUM CHLORIDE.

Table XXV.—Freezing Point Measurements.

<i>m.</i>	<i>P.</i>	<i>Δ.</i>	<i>m.</i>	<i>P.</i>	<i>Δ.</i>
0.3 CaCl ₂	I	1° .553	1.7 CaCl ₂	I	13° .50
0.3 MgCl ₂	I		1.7 MgCl ₂	I	
0.5 CaCl ₂	I	2° .704	2.1 CaCl ₂	I	19° .50
0.5 MgCl ₂	I		2.1 MgCl ₂	I	
0.7 CaCl ₂	I	4° .053	2.5 CaCl ₂	I	27° .25
0.7 MgCl ₂	I		2.5 MgCl ₂	I	
0.9 CaCl ₂	I	5° .543	2.9 CaCl ₂	I	37° .0
0.9 MgCl ₂	I		2.9 MgCl ₂	I	
1.3 CaCl ₂	I	9° .320			
1.3 MgCl ₂	I				

Table XXVI.—Conductivity Measurements.

<i>m.</i>	<i>P.</i>	<i>m.</i>	<i>V_c</i>	<i>k_u</i>	<i>k.</i>	<i>D.</i>	<i>k_c</i>	<i>A_v</i>	<i>a.</i>
0.3 CaCl ₂	I	0.15	6.6666	0.026923	0.014991	0.001711	0.014062	93.8	0.636
0.3 MgCl ₂	I	0.15	6.6666		0.013642		0.012861	85.7	0.664
0.5 CaCl ₂	I	0.25	4.000		0.024073		0.021709	86.8	0.505
0.5 MgCl ₂	I	0.25	4.000	0.041214	0.021529	0.004388	0.019505	78.0	0.605
0.7 CaCl ₂	I	0.35	2.8571		0.032700		0.028817	82.3	0.558
0.7 MgCl ₂	I	0.35	2.8571	0.053615	0.028240	0.007325	0.024798	70.9	0.549
0.9 CaCl ₂	I	0.45	2.2222		0.039688		0.033822	75.2	0.510
0.9 MgCl ₂	I	0.45	2.2222	0.065080	0.036183	0.010791	0.031258	69.5	0.538
1.3 CaCl ₂	I	0.65	1.538		0.054236		0.043256	66.9	0.454
1.3 MgCl ₂	I	0.65	1.538	0.082101	0.047864	0.019999	0.038575	59.3	0.460
1.7 CaCl ₂	I	0.85	1.1765		0.066903		0.050933	59.9	0.406
1.7 MgCl ₂	I	0.85	1.1765	0.094339	0.057606	0.03017	0.043406	51.1	0.396
2.1 CaCl ₂	I	1.05	0.9523		0.078244		0.055264	52.6	0.357
2.1 MgCl ₂	I	1.05	0.9523	0.10078	0.066286	0.04374	0.04552	43.4	0.336
2.5 CaCl ₂	I	1.25	0.8000		0.088853		0.057913	46.3	0.314
2.5 MgCl ₂	I	1.25	0.8000	0.10278	0.073499	0.05957	0.044869	35.9	0.278
2.9 CaCl ₂	I	1.45	0.68966		0.097385		0.058845	40.6	0.275
2.9 MgCl ₂	I	1.45	0.68966	0.10007	0.0978040	0.07536	0.04122	28.4	0.220

Table XXVII.—Weight-Normal Corrections.

<i>m.</i>	<i>P.</i>	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O.}	Correction per cent.
0.3 CaCl ₂	I	25.6460	0.77345	24.87255	0.5
0.3 MgCl ₂	I				
0.5 CaCl ₂	I	26.0314	1.28915	24.74225	1.0
0.5 MgCl ₂	I				
0.7 CaCl ₂	I	26.4594	1.80475	24.65465	1.4
0.7 MgCl ₂	I				
0.9 CaCl ₂	I	26.8453	2.32045	24.52485	1.9
0.9 MgCl ₂	I				
1.3 CaCl ₂	I	27.6088	3.35175	24.25705	3.0
1.3 MgCl ₂	I				
1.7 CaCl ₂	I	28.3821	4.38305	23.99905	4.0
1.7 MgCl ₂	I				
2.1 CaCl ₂	I	29.1096	5.41435	23.69525	5.2
2.1 MgCl ₂	I				
2.5 CaCl ₂	I	29.8333	6.44555	23.38775	6.5
2.5 MgCl ₂	I				
2.9 CaCl ₂	I	30.5280	7.47695	23.05105	8.8
2.9 MgCl ₂	I				

In Table XXVIII., m_c = normal concentration of each salt in the mixture. α = dissociation of each salt in the mixture, as given in Table XXVI. mL = lowering of freezing point, calculated from formula $[(1.86 \times 2\alpha) + 1.86]m$. The correction percentage is deduced on the assumption that the two salts form the same hydrates in the mixture that they form in separate solutions. Upon this assumption the amount of water which each salt would eliminate from the sphere of action as solvent is calculated from the formula

$$1,000 - \left[\frac{L}{\bar{L}}, \times 1,000 \right].$$

The values for magnesium chloride and calcium chloride are added together, and to this is added also the difference between 1000 grams and the amount of water actually present in one liter as given by the weight-normal corrections. This, then, is given as a percentage correction in the column headed "Correction, per cent." The value mL is divided by this percentage, and the result given under Δ .

Table XXVIII.

<i>m.</i>	<i>P.</i>	<i>m_c.</i>	<i>α.</i>	<i>mL.</i>	Correction, per cent.	<i>Δ.</i>
0.3 CaCl ₂	I	0.15	0.636	0°.634	78.9	0°.803
0.3 MgCl ₂	I		0.664	0°.650		0°.823
0.5 CaCl ₂	I		0.589	1°.012		1°.488
0.5 MgCl ₂	I	0.25	0.605	1°.027	68.0	1°.510
0.7 CaCl ₂	I		0.558	1°.378		2°.345
0.7 MgCl ₂	I		0.549	1°.366		2°.325
0.9 CaCl ₂	I	0.45	0.510	1°.690	51.2	3°.298
0.9 MgCl ₂	I		0.538	1°.738		3°.392
1.3 CaCl ₂	I		0.454	2°.360	38.5	5°.998
1.3 MgCl ₂	I	0.65	0.460	2°.321		6°.035
1.7 CaCl ₂	I		0.406	2°.865		1°.13
1.7 MgCl ₂	I	0.85	0.396	2°.832	25.81	11°.00
2.1 CaCl ₂	I		0.357	3°.346		22°.85
2.1 MgCl ₂	I		0.336	3°.264		22°.29

Evidently the sum of the values of Δ for calcium chloride and magnesium chloride, as thus found, should equal the lowering found experimentally for the mixture in question. These values are placed side by side, for comparison, in

Table XXIX.

<i>m.</i>	<i>P.</i>	<i>m_c.</i>	Δ (calculated).	Δ (Exp.).	Diff.
0.3 CaCl ₂	I	0.15	1°.626	1.553	0.073
0.3 MgCl ₂	I	0.15			
0.5 CaCl ₂	I	0.25	2°.998	2.704	0.294
0.5 MgCl ₂	I	0.25			
0.7 CaCl ₂	I	0.35	4°.670	4.053	0.617
0.7 MgCl ₂	I	0.35			
0.9 CaCl ₂	I	0.45	6°.690	5.543	1.147
0.9 MgCl ₂	I	0.45			
1.3 CaCl ₂	I	0.65	12°.033	9.320	2.713
1.3 MgCl ₂	I	0.65			
1.7 CaCl ₂	I	0.85	22°.13	13.5	8.629
1.7 MgCl ₂	I	0.85			
2.1 CaCl ₂	I	1.05	45°.14	19.5	25.64
2.1 MgCl ₂	I	1.05			

It is unnecessary to extend these calculations to the remaining, more concentrated mixtures, since it is evident that the differences between the values calculated on the basis that the two salts form the same hydrates in separate solutions

that they form in the mixtures and the values for Δ obtained experimentally become increasingly larger with increase in concentration. It is further evident that the hypothesis is untenable from the fact that it would call for the elimination of 944 grams of water per liter of solution in the case of the 2.5 N mixture of the above salts, and of 1047 grams in the case of the 2.9 N mixture.

At the moment of mixing the two solutions, each salt is prevented from forming the hydrate which it ordinarily forms in separate solution by the amount of water which has been eliminated from the sphere of action as solvent in the formation of the hydrate of the other component of the mixture. Consequently, for the more dilute solutions at least, the hydrates formed by a salt in separate solution should be related to the hydrates formed by the same salt in the mixture at corresponding concentrations as the amount of water present as solvent in the single solution is related to the amount present as solvent in the mixture. For example, take calcium chloride and magnesium chloride, 0.15 N solutions of each. Referring to Tables XX. and XXIV., if X represents the unknown value of M for calcium chloride, in the mixture $6 : X :: 1000 : 897$. 6.0 is the value of M for 0.15 N calcium chloride in separate solution, and this has been corrected to 1000 grams of solvent. The figure 897 is found by subtracting from 1000 the number of grams of water with which the magnesium chloride combines, when it forms the hydrate indicated for the concentration in question in Table XXIV., plus the difference between the amount of water present in the solution and 1000 grams, as given by the weight-normal correction.

Having thus obtained the values of M for the salts in the mixture, it is possible to solve for L' from the equation

$$M = \frac{1000 - \left[\frac{L}{L'} \times 1000 \right]}{18},$$

where L represents the theoretical lowering found for the salt by calculating it from the value of α , which has been de-

terminated for the mixture in question. This value of L' must then be corrected, in order to obtain the value as it would be observed, by dividing it by the proper per cent. This percentage correction is found by deducing the number of grams of water eliminated as water of hydration by the other salt in the mixture, basing the calculation upon the value of M worked out for the mixture. To this must be added the percentage correction which the weight-normal correction has given.

The sum of these values for L' for the two salts in the mixture should then be equal to Δ as found experimentally for the mixture, provided this hypothesis is correct. In the following tables the values thus obtained are given.

M_c = the value for M deduced from the proportion.

L'_c = the value for L' calculated upon this value of M .

$L'_c{}^{Cor.}$ = the value for L' , with proper percentage correction.

Sum = the sum of these two values for $L'_c{}^{Cor.}$, multiplied by the normality of the solution.

Δ = the lowering found experimentally for the same mixture.

The other symbols employed have the usual significance.

Without further extending this method of calculation, it is evident that it does not give the true value of the hydrates formed, and that the hydrating power is larger for the more concentrated mixtures than would be indicated by the proportions given below.

This is just what we should expect, for with increasing hydration we do not have the process of loss of water from the hydrates formed in separate solution going on to the end in the mixture, but instead, we have, necessarily, a condition of equilibrium between the hydrating powers of the two salts. Also, as a direct result, the amount of water thus left uncombined affects the final composition of the hydrates, as already indicated.

This condition of equilibrium is not represented by the proportions given above, since the amount of water playing the part of solvent is not that indicated by these proportions.

Table XXX.

$m.$	$P.$	$m_c.$	$M.$	$M_c.$	$L.$	$L'_c.$	$L'_c{}^{Cor.}$	Sum.	$\Delta.$
0.3 CaCl ₂	I	0.15	6.0	5.4	4.224	4.682	5.16	1° .57	1.553
0.3 MgCl ₂	I	0.15	5.5	4.9	4.330	4.748	5.29		
0.5 CaCl ₂	I	0.25	8.2	6.8	4.109	4.685	5.52	2° .74	2.704
0.5 MgCl ₂	I	0.25	9.2	7.8	4.050	4.715	5.44		
0.7 CaCl ₂	I	0.35	9.7	7.5	3.936	4.547	5.71	3° .97	4.053
0.7 MgCl ₂	I	0.35	12.7	10.5	3.902	4.808	5.64		
0.9 CaCl ₂	I	0.45	11.7	8.6	3.755	4.438	5.77	5° .26	5.543
0.9 MgCl ₂	I	0.45	14.9	11.8	3.862	4.897	5.92		
1.3 CaCl ₂	I	0.65	15.7	10.7	3.548	4.394	5.94	7° .74	9.32
1.3 MgCl ₂	I	0.65	17.8	12.8	3.570	4.639	5.97		
1.7 CaCl ₂	I	0.85	18.9	11.5	3.371	4.251	6.06	10° .21	13.5
1.7 MgCl ₂	I	0.85	21.7	14.3	3.332	4.487	5.96		

If we consider that the values of M for calcium chloride and for magnesium chloride in separate solutions, since their hydrating powers are nearly equal, represent the relative hydrating powers under the same conditions for the two salts, at the concentration corresponding to any pair of values of M , then it becomes possible to calculate the approximate composition of the hydrates of calcium chloride and magnesium chloride in the mixture. Selecting, for example, the mixture consisting of 1 part of 1.7 N calcium chloride and 1 part of 1.7 N magnesium chloride, then:

Let X equal the number of grams of water eliminated in the formation of the hydrate of calcium chloride which occurs in the mixture in question. If the hydrates of calcium chloride and magnesium chloride in the mixture are related as they are in separate solutions, they will be to each other as 18.9: 21.7 (see Tables XX. and XXIV.), hence,

$\frac{217}{189}X$ = the number of grams of water eliminated in the formation of hydrate of magnesium chloride in the mixture.

From the equation

$$M = \frac{1000 - \left[\frac{L}{L'} \times 1000 \right]}{18},$$

we have

$$X = 1000 - \frac{3371}{L'_{Ca}} \quad (1),$$

where 3.371 is the lowering found for 0.85 N calcium chloride by calculation from the value of α given in Table XXVI., and L'_{Ca} = the lowering observed for calcium chloride, corrected properly for water less than 1000 grams, and multiplied by m .

Similarly,

$$\frac{217}{189}X = 1000 - \frac{3332}{L'_{Mg}} \quad (2).$$

Let L'_O = *observed* lowering due to magnesium chloride. Then, $13^{\circ}.5 - L'_O$ = *observed* lowering due to calcium chloride (*vide* Table XXV.).

Then

$$L'_O = \frac{L'_{Mg} \times 0.85}{1 - \frac{X}{1000} - \frac{4}{100}} \quad (3),$$

where 0.85 is the normality in question, and the denominator is the necessary percentage correction, based upon the value of X and the correction given in Table XXVII.

Similarly,

$$13.5 - L'_O = \frac{L'_{Ca} \times 0.85}{1 - \frac{\frac{217}{189} X}{1000} - \frac{4}{100}} \quad (4).$$

From equation (1),

$$L'_{Ca} = \frac{3371}{1000 - X} \quad (5).$$

From equation (2),

$$L'_{Mg} = \frac{3332}{1.000 - 1.148 X} \quad (6).$$

Eliminating L'_O by combining equations (3) and (4), and then substituting the values of L'_{Ca} and L'_{Mg} from (5) and (6), it becomes possible to solve for X . By this method the values of M for calcium chloride and magnesium chloride in this mixture are found to be 17.1 and 19.6, respectively.

By the above methods the values of M for the mixtures between 0.9 N and 2.9 N have been derived, and are given in the following table, under M_c . The abbreviations at the top of each column have the usual significance, the suffix c indicating that the values are for the salt *in the mixture*.

For the sake of comparison, the values of M for calcium chloride and magnesium chloride in separate solutions are plotted as curves, against concentration (as axis of abscissas). Upon the same sheet are drawn similar curves for the values of M in the mixture.

Table XXXI.

$m.$	$P.$	$m_c.$	$\alpha.$	$L_c.$	$M.$	$\Delta.$	Sp Gr. Cor.	$M_c.$	$H_c.$
1.3 CaCl_2	1	0.65	0.454	3.548	15.74			14.5	22.3
1.3 MgCl_2	1	0.65	0.460	3.570	17.79	9.32	3.0	16.4	25.2
1.7 CaCl_2	1	0.85	0.406	3.371	18.92			17.1	20.1
1.7 MgCl_2	1	0.85	0.396	3.332	21.73	13.5	4.0	19.6	23.1
2.1 CaCl_2	1	1.05	0.357	3.187	21.92			19.8	18.9
2.1 MgCl_2	1	1.05	0.336	3.264	25.06	19.5	5.2	22.7	21.6
2.5 CaCl_2	1	1.25	0.314	3.028	24.32			22.8	18.2
2.5 MgCl_2	1	1.25	0.278	2.895	28.14	27.25	6.5	26.3	21.0
2.9 CaCl_2	1	1.45	0.275	2.883	27.29			25.9	17.9
2.9 MgCl_2	1	1.45	0.220	2.479	30.86	37.0	7.8	28.9	19.9

Upon comparing curve I., the hydration of magnesium chloride alone, with curve IV., the hydration of the calcium chloride in the mixture, it will be seen that where I. rises IV. falls, and *vice versa*. This is exactly what we should expect, since an increase in the hydrating power of magnesium chloride should result in a corresponding decrease in the amount

- I. *Magnesium Chloride Alone.*
- II. *Magnesium Chloride Mixed with Calcium Chloride.*
- III. *Calcium Chloride Alone.*
- IV. *Calcium Chloride Mixed with Magnesium Chloride.*

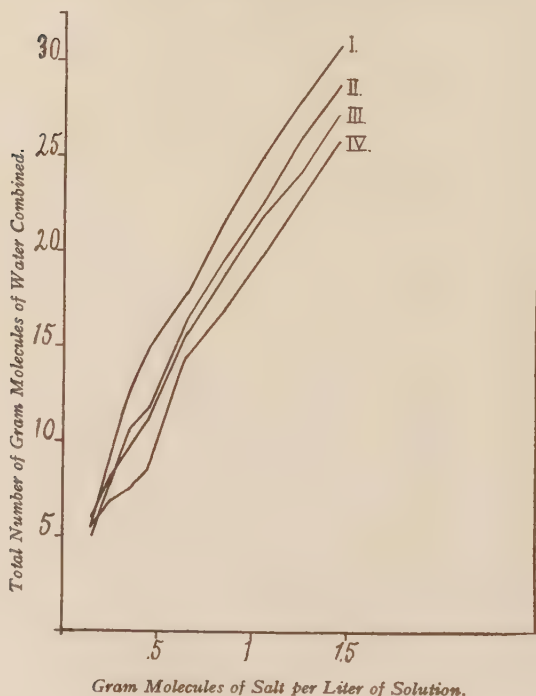


Fig. III.

of water with which the calcium chloride would be able to combine in the mixture, unless a corresponding increase in the hydrating power of the calcium chloride in separate solution should also occur. Again, comparing curves I. and II., and III. and IV., the hydrates in separate solution and in the

mixture are of the same general order of magnitude, except where the presence of the one salt in the mixture alters the composition of the hydrate formed by the other.

It was thought desirable to compare the effect of a salt with less hydrating power mixed with one of greater hydrating power.

For this purpose calcium chloride and strontium chloride were selected, the hydrating power of strontium chloride being somewhat less than that of calcium chloride

The data for the separate solutions of calcium chloride have already been given. Those of strontium chloride follow.

STRONTIUM CHLORIDE.

Table XXXII.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>m.</i>	Δ .	Δ/m .
0.15	0°.753	5.02	0.65	3°.521	5.42
0.25	1°.249	5.00	0.85	4°.863	5.72
0.35	1°.774	5.07	1.05	6°.354	6.05
0.45	2°.333	5.18	1.23541	7°.861	6.36

Table XXXIII.—Conductivity Measurements.

<i>m.</i>	<i>V.</i>	<i>k.</i>	Δv .	α .
0.15	6.6666	0.015377	102.5	0.747
0.25	4.0000	0.024185	96.7	0.705
0.35	2.8571	0.032590	93.1	0.678
0.45	2.2222	0.040479	90.0	0.655
0.65	1.5380	0.055017	84.6	0.616
0.85	1.1764	0.067824	79.8	0.581
1.05	0.9523	0.079796	76.0	0.553
1.23541	0.8945	0.088607	71.7	0.522

Table XXXIV.—Weight-Normal Corrections.

<i>m.</i>	<i>W_{sol.}</i>	<i>W_{salt.}</i>	<i>W_{H₂O.}</i>	Correction, per cent.
0.15	25.5325	0.59437	24.94810	0.3
0.25	25.8496	0.99060	24.85898	0.6
0.35	26.1900	1.38688	24.8031	0.8
0.45	26.5388	1.7831	24.7557	1.0
0.65	27.1944	2.5756	24.6188	1.5
0.85	27.8553	3.3681	24.4872	2.1
1.05	28.5672	4.1606	24.4066	2.4
1.23541	29.1297	4.8954	24.2344	3.1

Table XXXV.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.15	0.747	4.64	5.02	4.99	3.9	26.0
0.25	0.705	4.48	5.00	4.97	5.5	22.0
0.35	0.678	4.39	5.07	5.03	7.1	20.3
0.45	0.655	4.30	5.18	5.13	9.0	20.0
0.65	0.616	4.15	5.42	5.34	12.4	19.1
0.85	0.581	4.02	5.72	5.60	15.7	18.5
1.05	0.553	3.93	6.05	5.91	18.7	17.8
1.23541	0.522	3.80	6.36	6.17	21.3	17.2

MIXTURE OF CALCIUM CHLORIDE AND STRONTIUM CHLORIDE.

Table XXXVI.—Freezing Point Measurements.

<i>m.</i>	<i>P.</i>	Δ .	<i>m.</i>	<i>P.</i>	Δ .
0.3 CaCl ₂	I	1°.503	1.3 CaCl ₂	I	8°.682
0.3 SrCl ₂	I		1.3 SrCl ₂	I	
0.5 CaCl ₂	I	2°.626	1.7 CaCl ₂	I	12°.924
0.5 SrCl ₂	I		1.7 SrCl ₂	I	
0.7 CaCl ₂	I	3°.906	2.1 CaCl ₂	I	18°.290
0.7 SrCl ₂	I		2.1 SrCl ₂	I	
0.9 CaCl ₂	I	5°.310	2.5 CaCl ₂	I	Salt separated out.
0.9 SrCl ₂	I		2.5 SrCl ₂	I	

Table XXXVII.—Conductivity Measurements.

m .	P .	m_c .	V_c .	K_w .	k .	D .	k_c .	Λ_v .	α .
0.3 CaCl_2	1	0.15	6.6666	0.014991	0.028239	0.002129	0.013837	92.3	0.625
0.3 SrCl_2	1	0.15	6.6666	0.015377			0.014402	96.0	0.699
0.5 CaCl_2	1	0.25	4.0000	0.024073	0.043980	0.004278	0.021775	87.1	0.590
0.5 SrCl_2	1	0.25	4.0000	0.024185			0.022205	83.8	0.647
0.7 CaCl_2	1	0.35	2.8571	0.032700	0.051880	0.007102	0.028900	82.6	0.560
0.7 SrCl_2	1	0.35	2.8571	0.032590			0.029290	83.7	0.610
0.9 CaCl_2	1	0.45	2.2222	0.039688	0.070491	0.009676	0.034456	76.6	0.519
0.9 SrCl_2	1	0.45	2.2222	0.040479			0.036035	80.1	0.583
0.9 CaCl_2	1	0.65	1.5380	0.054236	0.090731	0.018522	0.044245	68.1	0.461
1.3 SrCl_2	1	0.65	1.5380	0.055017			0.046486	71.5	0.521
1.7 CaCl_2	1	0.85	1.1765	0.066903	0.105560	0.029177	0.051170	60.2	0.408
1.7 SrCl_2	1	0.85	1.1765	0.067824			0.054389	64.0	0.466
2.1 CaCl_2	1	1.05	0.9523	0.078244	0.114280	0.043760	0.054584	52.0	0.352
2.1 SrCl_2	1	1.05	0.9523	0.079796			0.059696	56.9	0.414

Table XXXVIII.—Weight-Normal Corrections.

<i>m.</i>		<i>P.</i>	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O}	Correction, per cent.
0.3	CaCl ₂	I	25.8463	1.0106	24.8357	0.7
0.3	SrCl ₂	I				
0.5	CaCl ₂	I	26.4106	1.6844	24.7262	1.1
0.5	SrCl ₂	I				
0.7	CaCl ₂	I	26.9452	2.3581	24.5871	1.7
0.7	SrCl ₂	I				
0.9	CaCl ₂	I	27.4711	3.0319	24.4392	2.2
0.9	SrCl ₂	I				
1.3	CaCl ₂	I	28.5671	4.3794	24.1877	3.3
1.3	SrCl ₂	I				
1.7	CaCl ₂	I	29.6381	5.7269	23.9112	4.4
1.7	SrCl ₂	I				
2.1	CaCl ₂	I	30.6744	7.0744	23.6031	5.6
2.1	SrCl ₂	I				

For the sake of comparison, the lowerings of the freezing point which would be obtained from the mixture of calcium chloride and strontium chloride are given in Table XXXIX., basing them upon the same method of calculation as that already given in detail for Table XXX. The symbols used have the same significance in the two tables.

It will be noted that in Table XXXIX., again, as in the case of the mixture of calcium chloride and magnesium chloride, the difference between the lowering as calculated upon the hypothesis that, for the more dilute solutions, at least, the hydrates formed by a salt in separate solution are related to the hydrates formed by the same salt in the mixture at corresponding concentrations as the amount of water present as solvent in the mixture—the difference between this and the lowering found experimentally becomes increasingly large. This has already been discussed in the preceding case.

The method of calculating the composition of the hydrates existing in a mixture of two salts with about the same hydrating power, such as calcium chloride and magnesium chloride, was based upon the assumption that the values of *M* in their separate solutions represent the relative hydrating powers under the same conditions for the two salts in their mixtures. While this applies where the hydrates formed are

Table XXXIX.

m_c	P	m_c	M	M_c	L	L/c	L/c^{coz}	Sum.	Δ
0.3 CaCl_2	1	0.15	6.0	5.6	4.186	4.65	5.00		
0.3 SrCl_2	1	0.15	3.9	3.5	4.461	4.76	5.32	1.548	1.503
0.5 CaCl_2	1	0.25	8.2	7.3	4.056	4.67	5.16		
0.5 SrCl_2	1	0.25	5.5	4.6	4.266	4.65	5.43	2.646	2.626
0.7 CaCl_2	1	0.35	9.7	8.3	3.942	4.63	5.26		
0.7 SrCl_2	1	0.35	7.1	5.7	4.127	4.60	5.51	3.771	3.906
0.9 CaCl_2	1	0.45	11.7	9.5	3.791	4.57	5.36		
0.9 SrCl_2	1	0.45	9.0	6.9	4.030	4.60	5.70	4.979	5.370
1.3 CaCl_2	1	0.65	15.7	11.7	3.576	4.53	5.56		
1.3 SrCl_2	1	0.65	12.4	8.5	3.797	4.48	5.92	7.465	8.682
1.7 CaCl_2	1	0.85	18.9	12.8	3.378	4.39	5.61		
1.7 SrCl_2	1	0.85	15.7	9.7	3.593	4.35	6.00	9.877	12.924
2.1 CaCl_2	1	1.05	21.9	13.3	3.171	4.17	5.49		
2.1 SrCl_2	1	1.05	18.7	10.3	3.40	4.17	5.92	11.99	18.290

of approximately the same degree of complexity, it would involve an error in the case of two salts of very different hydrating powers. For, if the power of forming hydrates, *i. e.*, of eliminating water from the sphere of action as solvent, differs, then, when two such substances are mixed, if a decrease in the amount of water eliminated from the sphere of action as solvent occurs, this decrease must be assigned to the two salts inversely as their values of M in separate solutions. This follows from a consideration of the fact that the salt with greater hydrating power will have, consequently, greater power of dehydrating the salt with lesser hydrating power. Therefore, the salt which has less power to unite with water must suffer the greater loss in water of hydration in the presence of the salt with stronger hydrating power.

Upon this assumption the following method of calculating the approximate composition of the hydrates in such a mixture has been worked out. Take the case of a mixture consisting of one volume of 0.3 N strontium chloride and one volume of 0.3 N calcium chloride:

Let X equal the total decrease in the number of grams of water eliminated from the sphere of action as solvent in the mixture, as compared with that eliminated in the separate solutions.

Then $\frac{39}{99} X$ = the diminution in the number of grams of water eliminated by the calcium chloride, and $\frac{60}{99} X$ = the diminution in the number of grams of water eliminated by the strontium chloride (see Tables XX. and XXXV. for the values of M in separate solutions).

108.5 grams of water were eliminated by the calcium chloride as water of hydration in the 0.15 N separate solution of that salt (see Table XX.). 70.5 grams were eliminated by the strontium chloride (see Table XXXV.). Therefore,

$$108.5 - 0.39X = 1000 - \frac{4186}{L'_{Ca}} \quad (1),$$

and

$$70.5 - 0.61X = 1000 - \frac{4461}{L'_{Sr}} \quad (2).$$

$$L'_{Ca} = \frac{4186}{891.5 + 0.39X}, \text{ and } L'_{Sr} = \frac{4461}{929.5 + 0.61X}.$$

Let L'_O = observed lowering for calcium chloride in the mixture, then,

$$L'_O = \frac{4186 \times 0.15}{891.5 + 0.39X} \div \frac{922.5 + 0.61X}{1000} \quad (3), \text{ and}$$

$$1.503 - L'_O = \frac{4461 \times 0.15}{929.5 + 0.61X} \div \frac{884.5 + 0.39X}{1000} \quad (4).$$

Combining equations (3) and (4),

$$1.503 = \frac{4186 \times 0.15}{822 + 0.904X + .0002379X^2} + \frac{4461 \times 0.15}{822 + 0.902X + 0.0002379X^2}.$$

From this equation the approximate value of X can be obtained. The values of M and H for the mixture of calcium chloride and strontium chloride, thus obtained, are given in Table XL. The symbols have the usual significance.

For the sake of comparison, the values of M for the separate solutions of calcium chloride and strontium chloride and those for the mixture of the two salts have been plotted as curves in Fig. IV.

We find that the results expressed in Fig. IV. are of the same character as those shown in Fig. III. for the mixture of calcium chloride and magnesium chloride. The curve of hydration of each salt in the mixture is parallel to the curve of its hydration in the single solution, except where large values, as shown in curve I., for calcium chloride alone have produced a corresponding lessening in the amount of water with which the strontium chloride has been able to unite in the mixture at a normality of 0.15 to 0.35. An increase in the hydrating power of the calcium chloride must necessarily be accompanied by a corresponding decrease in the complexity of the hydrates of strontium chloride.

In order to compare the difference in the amount of water present as solvent in the single solution and in the mixture with the difference in the value of M in the two cases, these

values are tabulated. D_{H_2O} is the difference in the amount of water present as solvent in the separate solution and in the mixture. It is found for a given salt by adding to the number of grams of water eliminated as water of hydration

- I. Calcium Chloride Alone.
- II. Calcium Chloride Mixed with Strontium Chloride.
- III. Strontium Chloride Alone.
- IV. Strontium Chloride Mixed with Calcium Chloride.

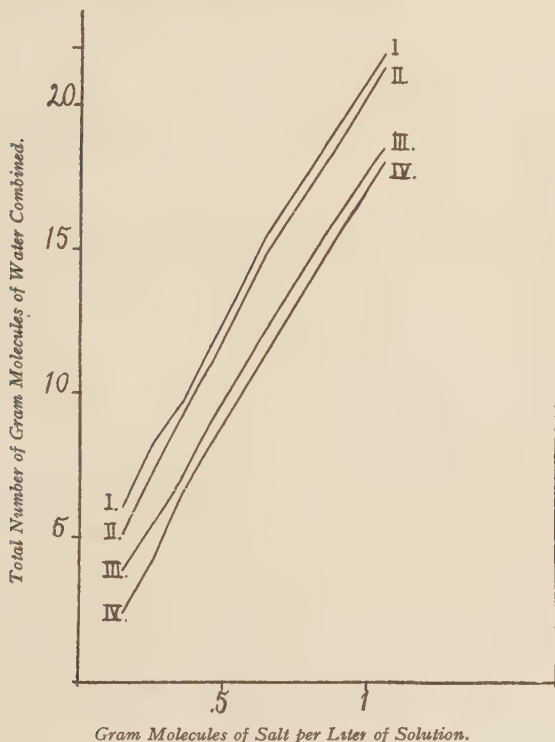


Fig. IV.

by the other salts in the mixture the difference between the correction to weight-normal standard in the case of the separate solution of the salt in question and in the mixture. D_m is the difference between the value of M in the single solution and in the mixture.

Table XLI.—Calcium Chloride in the Mixture of Calcium Chloride and Strontium Chloride.

<i>m.</i>	<i>DH₂O.</i>	<i>D_m.</i>	<i>m.</i>	<i>DH₂O.</i>	<i>D_m.</i>
0.15	46	0.9	0.65	226	0.6
0.25	81	0.9	0.85	295	0.6
0.35	127	0.4	1.05	359	0.4
0.45	162	0.6			

Table XLII.—Strontium Chloride in the Mixture of Calcium Chloride and Strontium Chloride.

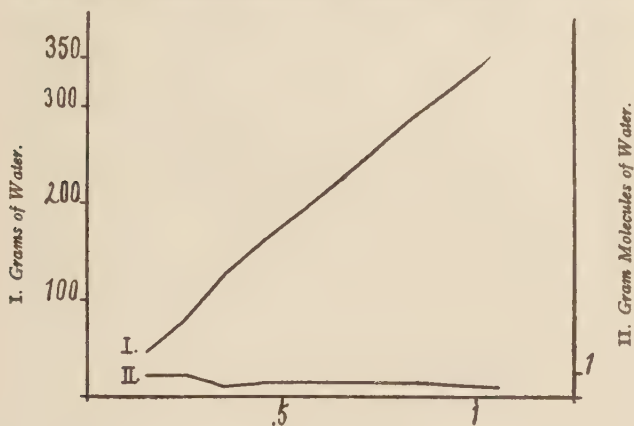
<i>m.</i>	<i>DH₂O.</i>	<i>D_m.</i>	<i>m.</i>	<i>DH₂O.</i>	<i>D_m.</i>
0.15	96	1.5	0.65	289	0.8
0.25	137	1.3	0.85	353	0.7
0.35	176	0.6	1.05	419	5.0
0.45	212	0.7			

These values are plotted as curves in Figs. V. and VI. The concentrations are the abscissas, and for curve I. the grams of water are taken as ordinates. In curve II. gram molecules of water form the ordinates.

It is readily seen from a comparison of the curves that the decrease in the amount of water present as solvent in the mixture is not accompanied by a corresponding decrease in the values of *M*. Here again, as in the case of the mixture of calcium chloride and potassium chloride, the difference in the values of *M* is nearly constant, because the concentration of both salts present in the mixture is increased at the same rate. Slight changes might be manifest if the ions and molecules have different hydrating powers, as seems very probable. Then a decrease in the number of ions and a correspondingly large increase in the number of molecules of dissolved substance present, such as necessarily occurs owing to suppression of the ionization in the mixture, would be accompanied by a change in the number of grams of water combined. That this plays a part in the change noted seems very probable.

For purposes of comparison these same values are given for a few concentrations in the case of calcium chloride and magnesium chloride. The phenomena are of the same kind.

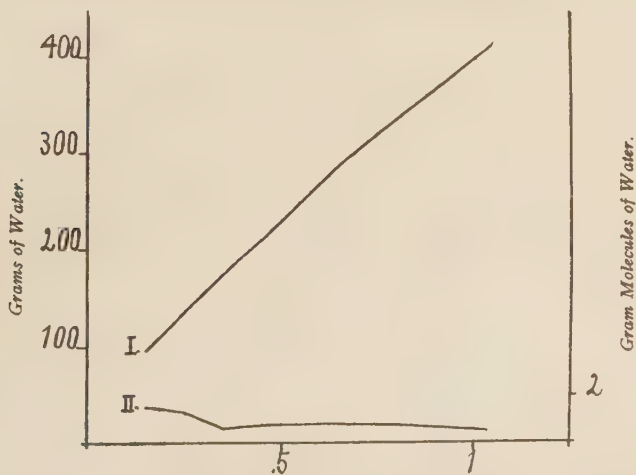
- I. Difference between Water Present as Solvent in Single Solution of Calcium Chloride and in Mixture of Calcium Chloride and Strontium Chloride.
 II. Difference between the Values of M for Calcium Chloride in Single Solution and in the Mixture of Calcium Chloride and Strontium Chloride.



Gram Molecules of Salt per Liter of Solution.

Fig. V.

- I. Difference between Water Present as Solvent in Single Solution of Strontium Chloride and in Mixture of Calcium Chloride and Strontium Chloride.
 II. Difference between the Values of M for Strontium Chloride in Single Solution and in the Mixture of Calcium Chloride and Strontium Chloride.



Gram Molecules of Salt per Liter of Solution.

Fig. VI.

Table XLIII.—Calcium Chloride in Calcium Chloride and Magnesium Chloride Mixture.

<i>m.</i>	D_{H_2O} .	D_m .	<i>m.</i>	D_{H_2O} .	D_m .
0.65	310.2	1.2	1.25	507.0	1.5
0.85	373.8	1.8	1.45	562.2	1.4
1.05	435.0	2.1			

Table XLIV.—Magnesium Chloride in Calcium Chloride and Magnesium Chloride Mixture.

<i>m.</i>	D_{H_2O} .	D_m .	<i>m.</i>	D_{H_2O} .	D_m .
0.65	279	1.4	1.25	450	1.8
0.85	333	2.1	1.45	512	2.0
1.05	389	2.4			

A pair of nitrates was next studied.

The salts must be of such a nature as not to unite to form complexes when mixed, and must have hydrating power. Magnesium nitrate and strontium nitrate were selected. The data for these two salts follow:

MAGNESIUM NITRATE.

Table XLV.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>M.</i>	Δ .	Δ/m .
0.15	0°.749	4.99	0.55	3°.019	5.49
0.25	1°.252	5.01	0.65	3°.669	5.64
0.35	1°.805	5.16	0.75	4°.393	5.86
0.45	2°.395	5.32			

Table XLVI.—Conductivity Measurements.

$$\Lambda_{\infty} 0^\circ = 128.5.$$

<i>m.</i>	<i>V.</i>	<i>k.</i>	Λ_v .	α .
0.15	6.6666	0.013701	91.3	0.711
0.25	4.0000	0.021563	86.3	0.671
0.35	2.8571	0.028613	81.8	0.636
0.45	2.2222	0.035123	78.1	0.607
0.55	1.8182	0.041506	75.5	0.587
0.65	1.5380	0.046942	72.2	0.562
0.75	1.3333	0.052260	69.7	0.542

Table XLVII.—Weight-Normal Corrections.

<i>m.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.15	25.4306	0.5567	24.8738	0.5
0.25	25.6880	0.9277	24.7603	1.0
0.35	25.9782	1.2989	24.6794	1.3
0.45	26.2075	1.6610	24.5376	1.8
0.55	26.4748	2.0411	24.4338	2.3
0.65	26.7605	2.4122	24.3484	2.6
0.75	27.0203	2.7833	24.2371	3.1

Table XLVIII.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\Delta/m.$	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.15	0.711	4.50	4.99	4.97	5.3	35.1
0.25	0.671	4.36	5.01	4.96	6.7	26.9
0.35	0.636	4.23	5.16	5.09	9.4	26.8
0.45	0.607	4.12	5.32	5.22	11.7	26.0
0.55	0.587	4.05	5.49	5.36	13.6	24.7
0.65	0.562	3.95	5.68	5.49	15.6	24.0
0.75	0.542	3.88	5.86	5.68	17.6	23.5

STRONTIUM NITRATE.

Table XLIX.—Freezing Point Measurements.

<i>m.</i>	$\Delta.$	$\Delta/m.$	<i>m.</i>	$\Delta.$	$\Delta/m.$
0.15	0°.674	4.49	0.55	2°.286	4.16
0.25	1°.085	4.34	0.65	2°.681	4.12
0.35	1°.516	4.33	0.75	3°.060	4.08
0.45	1°.903	4.23			

Table L.—Conductivity Measurements.

$$\Lambda_{\infty} 0^{\circ} = 134.4.$$

<i>m.</i>	<i>V.</i>	<i>k.</i>	Λv_0	<i>α.</i>
0.15	6.6666	0.013164	87.8	0.653
0.25	4.0000	0.019905	79.6	0.592
0.35	2.8571	0.025748	73.6	0.548
0.45	2.2222	0.030645	68.1	0.507
0.55	1.8182	0.035106	63.8	0.475
0.65	1.5380	0.038936	59.9	0.446
0.75	1.3333	0.042076	56.1	0.417

Table LI.—Weight-Normal Corrections.

<i>m.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.15	25.6245	0.7938	24.8307	0.7
0.25	26.0440	1.3542	24.6898	1.2
0.35	26.4408	1.8960	24.5449	1.8
0.45	26.8623	2.4376	24.4247	2.3

Table LI—(Continued).

<i>m.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.55	27.2890	2.9793	24.3097	2.8
0.65	27.0907	3.5210	24.1697	3.3
0.75	28.0818	4.0627	24.0191	3.9

Table LII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.15	0.653	4.29	4.49	4.46	2.1	14.1
0.25	0.592	4.06	4.34	4.29	2.98	11.9
0.35	0.548	3.80	4.33	4.25	4.6	13.2
0.45	0.507	3.75	4.23	4.13	5.1	11.4
0.55	0.475	3.63	4.16	4.04	5.6	10.3
0.65	0.446	3.52	4.12	3.98	6.4	9.9
0.75	0.417	3.41	4.08	3.92	7.2	9.6

The data for the *mixture* of magnesium nitrate and strontium nitrate follow:

Table LIII.—Freezing Point Measurements.

<i>m.</i>	<i>P.</i>	Δ .	<i>m.</i>	<i>P.</i>	Δ .
0.3 Mg(NO ₃) ₂	I	1°.394	1.1 Mg(NO ₃) ₂	I	5°.646
0.3 Sr(NO ₃) ₂	I		1.1 Sr(NO ₃) ₂	I	
0.5 Mg(NO ₃) ₂	I	2°.351	1.3 Mg(NO ₃) ₂	I	6°.893
0.5 Sr(NO ₃) ₂	I		1.3 Sr(NO ₃) ₂	I	
0.7 Mg(NO ₃) ₂	I	3°.371	1.5 Mg(NO ₃) ₂	I	8°.169
0.7 Sr(NO ₃) ₂	I		1.5 Sr(NO ₃) ₂	I	
0.9 Mg(NO ₃) ₂	I	4°.573			
0.9 Sr(NO ₃) ₂	I				

Table LIV.—Weight-Normal Corrections.

<i>m.</i>	<i>P.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.3 Mg(NO ₃) ₂	I	26.044	1.3505	24.6936	1.2
0.3 Sr(NO ₃) ₂	I				
0.5 Mg(NO ₃) ₂	I	26.7087	2.2819	24.4268	2.3
0.5 Sr(NO ₃) ₂	I				
0.7 Mg(NO ₃) ₂	I	27.3970	3.1948	24.2022	3.2
0.7 Sr(NO ₃) ₂	I				
0.9 Mg(NO ₃) ₂	I	28.0570	4.1076	23.9435	4.2
0.9 Sr(NO ₃) ₂	I				
1.1 Mg(NO ₃) ₂	I	28.6884	5.0208	23.6681	5.3
1.1 Sr(NO ₃) ₂	I				
1.3 Mg(NO ₃) ₂	I	29.3508	5.9332	23.4177	6.3
1.3 Sr(NO ₃) ₂	I				
1.5 Mg(NO ₃) ₂	I	29.9912	6.8460	23.1452	7.4
1.5 Sr(NO ₃) ₂	I				

Table LV.—Conductivity Measurements

<i>m.</i>	<i>P.</i>	<i>m_c.</i>	<i>V_c.</i>	<i>k_u.</i>	<i>k_s.</i>	<i>D.</i>	<i>k_c.</i>	<i>Λ_v.</i>	<i>α.</i>
0.3 Mg(NO ₃) ₂	I	0.15	6.6666	0.023842	0.013701	0.003023	0.012288	81.9	0.638
0.3 Sr(NO ₃) ₂	I	0.15	6.6666		0.013164		0.011555	77.0	0.573
0.5 Mg(NO ₃) ₂	I	0.25	4.0000	0.035522	0.021563	0.005946	0.018843	75.4	0.587
0.5 Sr(NO ₃) ₂	I	0.25	4.0000		0.019905		0.016681	66.7	0.497
0.7 Mg(NO ₃) ₂	I	0.35	2.8571	0.044660	0.028613	0.009701	0.024231	69.2	0.539
0.7 Sr(NO ₃) ₂	I	0.35	2.8571		0.025748		0.020429	58.4	0.434
0.9 Mg(NO ₃) ₂	I	0.45	2.2222	0.051704	0.035123	0.014064	0.028881	64.2	0.500
0.9 Sr(NO ₃) ₂	I	0.45	2.2222		0.030645		0.022829	50.7	0.378
1.1 Mg(NO ₃) ₂	I	0.55	1.8182	0.057068	0.041506	0.019526	0.032987	60.0	0.467
1.1 Sr(NO ₃) ₂	I	0.55	1.8182		0.035106		0.024096	43.8	0.326
1.3 Mg(NO ₃) ₂	I	0.65	1.538	0.060997	0.046042	0.024881	0.036202	55.7	0.433
1.3 Sr(NO ₃) ₂	I	0.65	1.538		0.038936		0.024786	38.1	0.284
1.5 Mg(NO ₃) ₂	I	0.75	1.3333	0.063788	0.052260	0.030548	0.039310	52.4	0.408
1.5 Sr(NO ₃) ₂	I	0.75	1.3333		0.042076		0.024476	32.6	0.243

Table LVI.—Hydrates.

<i>m.</i>	<i>F.</i>	<i>mc.</i>	α .	<i>Lc.</i>	<i>M.</i>	Δ .	Sp. Gr. Cor.	<i>Mc.</i>	<i>Hc.</i>
0.3 $\text{Mg}(\text{NO}_3)_2$	I	0.15	0.638	4.231	5.3	1.394	1.2	4.9	32.5
0.3 $\text{Sr}(\text{NO}_3)_2$	I	0.15	0.573	3.992	2.1			1.0	6.6
0.5 $\text{Mg}(\text{NO}_3)_2$	I	0.25	0.587	4.042	6.7	2.351	2.3	6.5	26.0
0.5 $\text{Sr}(\text{NO}_3)_2$	I	0.25	0.497	3.707	3.0			2.4	9.6
0.7 $\text{Mg}(\text{NO}_3)_2$	I	0.35	0.539	3.864	9.4	3.371	3.2	8.8	25.1
0.7 $\text{Sr}(\text{NO}_3)_2$	I	0.35	0.434	3.476	4.6			3.4	9.6
0.9 $\text{Mg}(\text{NO}_3)_2$	I	0.45	0.500	3.718	11.7	4.513	4.2	11.4	25.3
0.9 $\text{Sr}(\text{NO}_3)_2$	I	0.45	0.378	3.264	5.1			4.4	9.8
1.1 $\text{Mg}(\text{NO}_3)_2$	I	0.55	0.467	3.596	13.6	5.646	5.3	13.3	24.2
1.1 $\text{Sr}(\text{NO}_3)_2$	I	0.55	0.326	3.073	5.6			4.9	8.8
1.3 $\text{Mg}(\text{NO}_3)_2$	I	0.65	0.433	3.472	15.6	6.892	6.3	15.2	23.4
1.3 $\text{Sr}(\text{NO}_3)_2$	I	0.65	0.284	2.915	6.4			5.5	8.5
1.5 $\text{Mg}(\text{NO}_3)_2$	I	0.75	0.408	3.377	17.6	8.169	7.4	17.0	22.7
1.5 $\text{Sr}(\text{NO}_3)_2$	I	0.75	0.243	2.763	7.2			5.7	7.6

The values of M for this mixture are calculated by the method already given. Evidently the same method of calculation applies here as in the case of a mixture of calcium chloride and strontium chloride.

The values of M , in single solution and in the mixture, for magnesium nitrate and strontium nitrate have been plotted as curves in Fig. VII. The phenomena are, in general, the

- I. *Magnesium Nitrate Alone.*
- II. *Magnesium Nitrate Mixed with Strontium Nitrate.*
- III. *Strontium Nitrate Alone.*
- IV. *Strontium Nitrate Mixed with Magnesium Nitrate.*

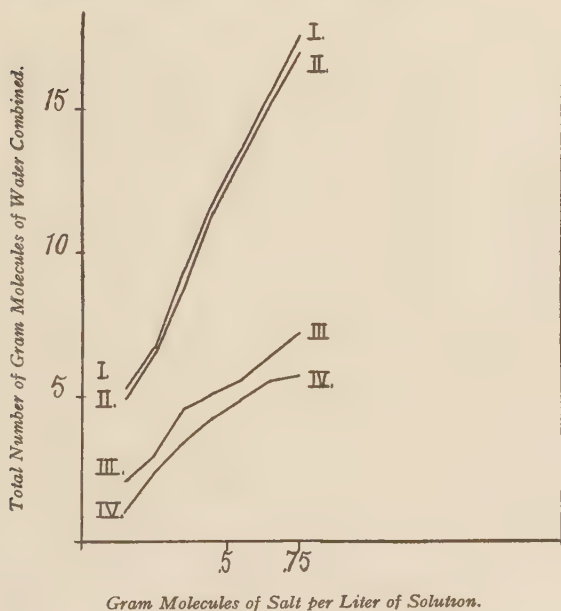


Fig. VII.

same as those already pointed out in preceding cases. Curve IV. deviates from curve III. with increasing concentration, showing the effect of the large increase in the value of M for magnesium nitrate, with increasing concentration, upon the amount of water eliminated as water of hydration by the strontium nitrate. The strontium nitrate is dehydrated, partially, by the magnesium nitrate.

In Tables LVII. and LVIII., we have the differences in the amount of solvent present and in the values of M , as previously described for the corresponding tables.

Table LVII.—Magnesium Nitrate in Mixture of Magnesium Nitrate and Strontium Nitrate.

<i>m.</i>	$DH_2O.$	$Dm.$	<i>m.</i>	$DH_2O.$	$Dm.$
0.15	25	0.4	0.55	118	0.3
0.25	56	0.2	0.65	136	0.4
0.35	80	0.6	0.75	146	0.6
0.45	103	0.3			

Table LVIII.—Strontium Nitrate in Mixture of Magnesium Nitrate and Strontium Nitrate.

<i>m.</i>	$DH_2O.$	$Dm.$	<i>m.</i>	$DH_2O.$	$Dm.$
0.15	93	1.1	0.55	264	0.7
0.25	128	0.6	0.65	304	0.9
0.35	172	1.3	0.75	341	1.5
0.45	224	0.7			

In Figs. VIII. and IX. these values are plotted as curves.

We have here, again, a uniform decrease in the amount of water present as solvent, showing a uniform increase in the hydration with increase in concentration. The curves showing the differences in the values of M correspond to a constant difference in the amount of water eliminated in single solution and in the mixture. This constant difference is, of course, due to the fact that the concentration of both salts in the mixture is increased uniformly. The curves show, also, that this difference is slightly affected by the difference in the amount of water present as solvent, since they show a tendency to increase as the diminution in water present as solvent becomes greater.

We next took up a pair of binary electrolytes, LITHIUM BROMIDE and SODIUM BROMIDE, neither of which has a very large hydrating power, the hydrating power of the sodium bromide being somewhat less than that of the lithium bromide.

- I. Difference between Water Present as Solvent in the Single Solution of Magnesium Nitrate and in Mixture of Magnesium Nitrate and Strontium Nitrate.
 II. Difference between Values of M for Magnesium Nitrate in Single Solution and in the Mixture of Magnesium Nitrate and Strontium Nitrate.

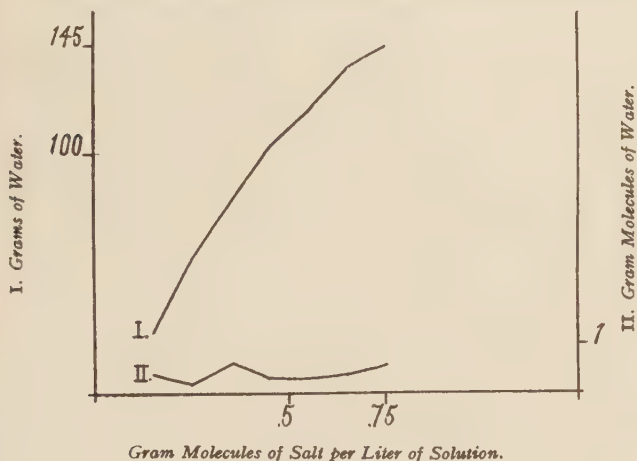


Fig. VIII.

- I. Difference between the Amount of Water Present as Solvent in the Single Solution of Strontium Nitrate and in the Mixture of Magnesium Nitrate and Strontium Nitrate.
 II. Difference between the Values of M for Strontium Nitrate in Single Solution and in the Mixture of Magnesium Nitrate and Strontium Nitrate.

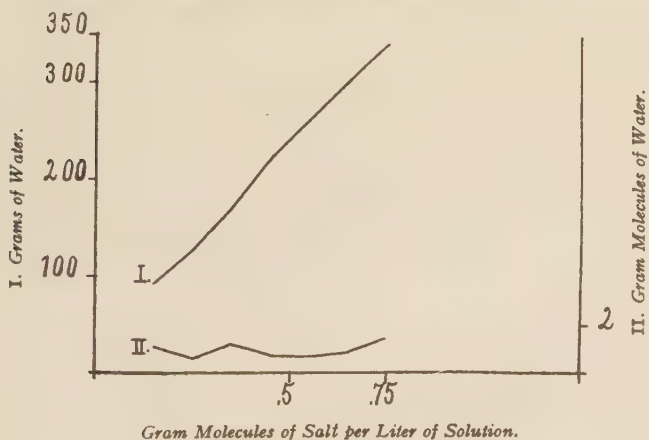


Fig. IX.

SODIUM BROMIDE.

Table LIX.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>m.</i>	Δ .	Δ/m .
0.25	0°.895	3.58	0.75	2°.691	3.59
0.35	1°.249	3.57	0.85	3°.054	3.59
0.45	1°.601	3.56	0.95	3°.435	3.62
0.55	1°.946	3.54	1.05	3°.839	3.66
0.65	2°.298	3.54			

Table LX.—Conductivity Measurements.

$\Lambda_{\infty} 0^{\circ} = 67.7.$				
<i>m.</i>	<i>V.</i>	<i>k.</i>	$\Lambda v.$	$\alpha.$
0.25	4.0000	0.014308	57.2	0.845
0.35	2.8571	0.019628	56.1	0.828
0.45	2.2222	0.024843	55.2	0.815
0.55	1.8182	0.029744	54.1	0.799
0.65	1.5380	0.034269	52.7	0.779
0.75	1.3333	0.039324	52.4	0.774
0.85	1.1765	0.044009	51.8	0.765
0.95	1.0526	0.048853	51.4	0.760
1.05	0.9523	0.053228	50.7	0.747

Table LXI.—Weight-Normal Corrections.

<i>m.</i>	<i>W</i> Sol.	<i>W</i> Salt.	<i>W</i> H ₂ O.	Correction, per cent.
0.25	25.4629	0.6438	24.8191	0.4
0.35	25.7300	0.9014	24.7987	0.8
0.45	25.8823	1.1589	24.7234	1.1
0.55	26.0735	1.4164	24.6571	1.4
0.65	26.2560	1.6727	24.5833	1.7
0.75	26.4535	1.9344	24.5221	1.9
0.85	26.6155	2.1890	24.4265	2.3
0.95	26.8260	2.4465	24.3795	2.5
1.05	27.0072	2.7040	24.3032	2.8

Table LXII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.25	0.845	3.43	3.58	3.55	1.9	7.6
0.35	0.828	3.40	3.57	3.54	2.2	6.3
0.45	0.815	3.38	3.56	3.52	2.2	4.9
0.55	0.799	3.35	3.54	3.49	2.2	4.0
0.65	0.779	3.31	3.54	3.48	2.7	4.2
0.75	0.774	3.30	3.59	3.52	3.5	4.6
0.85	0.765	3.28	3.59	3.51	3.6	4.2
0.95	0.760	3.27	3.62	3.53	4.1	4.3
1.05	0.747	3.25	3.66	3.56	4.8	4.6

LITHIUM BROMIDE.

Table LXIII.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>m.</i>	Δ .	Δ/m .
0.25	0°.917	3.67	0.75	2°.957	3.94
0.35	1°.292	3.69	0.85	3°.418	4.02
0.45	1°.679	3.75	0.95	3°.900	4.11
0.55	2°.090	3.80	1.05	4°.381	4.17
0.65	2°.514	3.87			

Table LXIV.—Conductivity Measurements.

<i>m.</i>	<i>V.</i>	<i>k.</i>	Δv .	α .
0.25	4.0000	0.012699	50.8	0.848
0.35	2.8571	0.017288	49.4	0.825
0.45	2.2222	0.021694	48.2	0.805
0.55	1.8182	0.025855	47.0	0.785
0.65	1.5380	0.029863	45.9	0.757
0.75	1.3333	0.033996	45.3	0.745
0.85	1.1765	0.057904	44.6	0.734
0.95	1.0526	0.041760	44.0	0.723
1.05	0.9523	0.045505	43.3	0.767

Table LXV.—Weight-Normal Corrections.

<i>m.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.25	25.3913	0.5437	24.8476	0.6
0.35	25.5641	0.7612	24.8029	0.8
0.45	25.7225	0.9786	24.7439	1.0
0.55	25.8690	1.1961	24.6729	1.3
0.65	26.0358	1.4136	24.6222	1.5
0.75	26.1585	1.6311	24.5274	1.9
0.85	26.3303	1.8485	24.4818	2.1
0.95	26.4558	2.0660	24.3898	2.4
1.05	26.6235	2.2835	24.3400	2.6

Table LXVI.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\Delta/m.$	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.25	0.848	3.44	3.67	3.65	3.2	12.8
0.35	0.825	3.39	3.69	3.63	3.7	10.6
0.45	0.805	3.36	3.75	3.71	5.2	11.6
0.55	0.785	3.32	3.80	3.75	6.4	11.6
0.65	0.767	3.29	3.87	3.81	7.5	11.5
0.75	0.757	3.27	3.94	3.87	8.6	11.5
0.85	0.745	3.25	4.02	3.94	9.7	11.4
0.95	0.734	3.23	4.11	4.01	10.8	11.4
1.05	0.723	3.21	4.17	4.06	11.6	11.0

MIXTURE OF LITHIUM BROMIDE AND SODIUM BROMIDE.

Table LXVII.—Freezing Point Measurements.

<i>m.</i>	<i>P.</i>	$\Delta.$	<i>m.</i>	<i>P.</i>	$\Delta.$
0.5 LiBr	I	1° .823	1.5 LiBr	I	6° .293
0.5 NaBr	I		1.5 NaBr	I	
0.7 LiBr	I	2° .596	1.7 LiBr	I	7° .328
0.7 NaBr	I		1.7 NaBr	I	
0.9 LiBr	I	3° .415	1.9 LiBr	I	8° .399
0.9 NaBr	I		1.9 NaBr	I	
1.1 LiBr	I	4° .325	2.1 LiBr	I	9° .539
1.1 NaBr	I		2.1 NaBr	I	
1.3 LiBr	I	5° .284			
1.3 NaBr	I				

Table LXVIII.—Conductivity Measurements.

<i>m.</i>	<i>P.</i>	<i>m_c</i>	<i>V_c</i>	<i>k_u</i>	<i>k.</i>	<i>D.</i>	<i>k_c</i>	<i>Δ_v</i>	<i>α.</i>
0.5 LiBr	1	0.25	4.0000	0.025489	0.012699	0.001518	0.011986	47.9	0.800
0.5 NaBr	1	0.25	4.0000		0.014308		0.013503	54.0	0.798
0.7 LiBr	1	0.35	2.8571	0.034327	0.017288	0.002589	0.016073	45.9	0.767
0.7 NaBr	1	0.35	2.8571		0.019628		0.018254	52.2	0.770
0.9 LiBr	1	0.45	2.2222	0.042727	0.021694	0.003810	0.019905	44.2	0.738
0.9 NaBr	1	0.45	2.2222		0.024843		0.022822	50.7	0.749
1.1 LiBr	1	0.55	1.8182	0.051105	0.025855	0.004494	0.023745	43.2	0.721
1.1 NaBr	1	0.55	1.8182		0.029744		0.027360	49.8	0.735
1.3 LiBr	1	0.65	1.538	0.058945	0.029863	0.005187	0.027248	42.2	0.704
1.3 NaBr	1	0.65	1.538		0.034269		0.031517	48.5	0.716
1.5 LiBr	1	0.75	1.3333	0.066486	0.037904	0.006834	0.030788	41.1	0.685
1.5 NaBr	1	0.75	1.3333		0.044009		0.035698	47.6	0.703
1.7 LiBr	1	0.85	1.1765	0.073132	0.04176	0.008781	0.033841	39.8	0.665
1.7 NaBr	1	0.85	1.1765		0.048853		0.039291	46.2	0.683
1.9 LiBr	1	0.95	1.0526	0.080414	0.045505	0.010199	0.03688	38.8	0.648
1.9 NaBr	1	0.95	1.0526		0.053228		0.043531	45.8	0.677
2.1 LiBr	1	1.05	0.9523	0.033996	0.033996	0.012086	0.039832	37.9	0.633
2.1 NaBr	1	1.05	0.9523	0.086647	0.039324		0.046815	44.6	0.659

Since lithium bromide and sodium bromide are each binary and dissociated to almost exactly the same extent at equal concentrations of the solutions, the loss in conductivity is apportioned to an equal driving back in the dissociation of the lithium bromide and sodium bromide, except in the mixtures $\left. \begin{smallmatrix} 1.7 \text{ LiBr} \\ 1.7 \text{ NaBr} \end{smallmatrix} \right\}$ and $\left. \begin{smallmatrix} 1.9 \text{ LiBr} \\ 1.9 \text{ NaBr} \end{smallmatrix} \right\}$, where the slight difference in the dissociation of the separate solutions is taken into account.

Table LXIX.—Weight-Normal Corrections.

<i>m.</i>	<i>P.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.5 LiBr	1				
0.5 NaBr	1	25.9003	1.18748	24.7128	1.1
0.7 LiBr	1				
0.7 NaBr	1	26.2462	1.6625	24.5837	1.7
0.9 LiBr	1				
0.9 NaBr	1	26.6053	2.1375	24.4678	2.1
1.1 LiBr	1				
1.1 NaBr	1	26.9317	2.6125	24.3192	2.7
1.3 LiBr	1				
1.3 NaBr	1	27.2984	3.0863	24.2121	3.2
1.5 LiBr	1				
1.5 NaBr	1	27.5978	3.5625	24.0353	3.9
1.7 LiBr	1				
1.7 NaBr	1	27.9400	4.0375	23.9025	4.4
1.9 LiBr	1				
1.9 NaBr	1	28.2890	4.5125	23.7765	4.9
2.1 LiBr	1				
2.1 NaBr	1	28.6065	4.9875	23.6190	5.5

Table LXX.—Hydrates.

<i>m.</i>	<i>m_c.</i>	<i>α.</i>	<i>L_c.</i>	<i>M.</i>	<i>Δ.</i>	Sp. Gr. Cor.	<i>M_c.</i>	<i>H_c.</i>
0.5 LiBr	0.25	0.800	3.349	3.2			8.2	11.2
0.5 NaBr	0.25	0.798	3.344	1.9	1.823	1.1	2.1	4.8
0.7 LiBr	0.35	0.767	3.286	3.7			3.5	10.0
0.7 NaBr	0.35	0.770	3.293	2.2	2.596	1.7	2.0	5.7
0.9 LiBr	0.45	0.738	3.233	5.2			5.2	11.5
0.9 NaBr	0.45	0.749	3.253	2.2	3.415	2.1	2.0	4.5
1.1 LiBr	0.55	0.721	3.201	6.4			6.7	12.2
1.1 NaBr	0.55	0.735	3.227	2.2	4.325	2.7	2.3	4.2
1.3 LiBr	0.65	0.704	3.107	7.5			8.0	12.3
1.3 NaBr	0.65	0.716	3.192	2.7	5.284	3.2	2.9	4.5
1.5 LiBr	0.75	0.685	3.135	8.6			8.9	11.8
1.5 NaBr	0.75	0.703	3.168	3.5	6.293	3.9	3.6	4.8

P = 1 in every case.

Table LXX.—(Continued).

<i>m.</i>	<i>m_c.</i>	<i>α.</i>	<i>L_c.</i>	<i>M.</i>	<i>Δ.</i>	Sp. Gr. Cor.	<i>M_c.</i>	<i>H_c.</i>
1.7 LiBr	0.85	0.665	3.096	9.7			10.2	12.0
1.7 NaBr	0.85	0.683	3.130	3.6	7.328	4.4	3.8	4.4
1.9 LiBr	0.95	0.648	3.065	10.8			11.0	11.6
1.9 NaBr	0.95	0.677	3.119	4.1	8.399	4.9	4.2	4.4
2.1 LiBr	1.05	0.633	3.038	11.6			11.6	11.0
2.1 NaBr	1.05	0.659	3.085	4.8	9.539	5.5	4.8	4.6

P — equals 1 in every case.

The values of *M* and *H* for this mixture are calculated upon the same basis as that previously employed in the mixture of magnesium nitrate and strontium nitrate. The values thus obtained for the mixture of lithium bromide and sodium bromide are given in the following table:

Curve II., Fig. X., representing the value of *M* in the mixture of lithium bromide and sodium bromide, crosses curve

- I. Lithium Bromide Alone.
- II. Lithium Bromide Mixed with Sodium Bromide.
- III. Sodium Bromide Alone.
- IV. Sodium Bromide Mixed with Lithium Bromide.

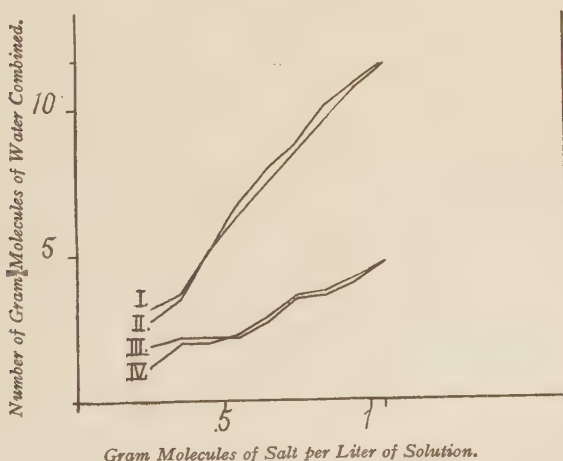


Fig. X.

I., the value of *M* for lithium bromide in single solution. The same phenomena presents itself in the case

of sodium bromide at a somewhat greater concentration. In an earlier part of this paper it was suggested that the hydrating power of the ions alone and of these ions when combined to form molecules would probably be different. If, now, the hydrating power of the lithium bromide and the sodium bromide molecules is greater than that of the respective ions, we might expect that the effect of the smaller amount of water present as solvent in the mixture would be overcome by the greater hydrating power of the undissociated molecules. Evidently, for this increased hydrating power of the molecules over the ions to show itself in the resulting curve, the other salt in the mixture must have little hydrating power and a comparatively small molecular weight, for if the molecular weight is large, so much solvent will be displaced when the solutions are made up volume normal that the decreased amount of solvent will obscure any change in hydration due to other causes. Also, the difference in the hydrating power of the ions and molecules should be considerable, in order to overcome the effect of decrease in amount of solvent present with increase in concentration.

The difference between the amount of water acting as solvent towards each salt in the mixture and in single solution, and the differences between the values of M in the same cases, are given in the following tables. A negative value of D_m indicates that the number of grams of water eliminated by a salt in a mixture is greater, instead of less, than in single solution.

Table LXXI.—Lithium Bromide in Mixture of Lithium Bromide and Sodium Bromide.

$m.$	$D_{H_2O}.$	$D_m.$	$m.$	$D_{H_2O}.$	$D_m.$
0.25	27	0.4	0.75	85	—0.3
0.35	45	0.2	0.85	91	—0.3
0.45	47	0.0	0.95	101	—0.2
0.55	55	—0.3	1.05	115	0.0
0.65	69	—0.5			

Table LXXII.—Sodium Bromide in Mixture of Lithium Bromide and Sodium Bromide.

m .	D_{H_2O} .	D_m .	m .	D_{H_2O} .	D_m .
0.25	54	0.7	0.75	180	—1.1
0.35	72	0.2	0.85	205	—0.2
0.45	104	0.2	0.95	222	—0.1
0.55	134	—0.1	1.05	236	0.0
0.65	159	—0.2			

These values are plotted as curves in Figs. XI. and XII. The fact that the curves show positive values of D_m has already been explained as probably due to the increased hydrating power of the molecule over its ions, so that when sufficient driving back in dissociation occurs we would get an increased amount of water eliminated as water of hydration. That this difference is nearly constant is to be expected, since corresponding additions of sodium bromide and lithium bromide are always made in changes of concentration.

- I. Difference between the Amount of Water Present as Solvent in the Single Solution of Lithium Bromide and in the Mixture of Lithium Bromide and Sodium Bromide.
 II. Differences between the Values of M for Lithium Bromide in Single Solution and in the Mixture of Lithium Bromide and Sodium Bromide.

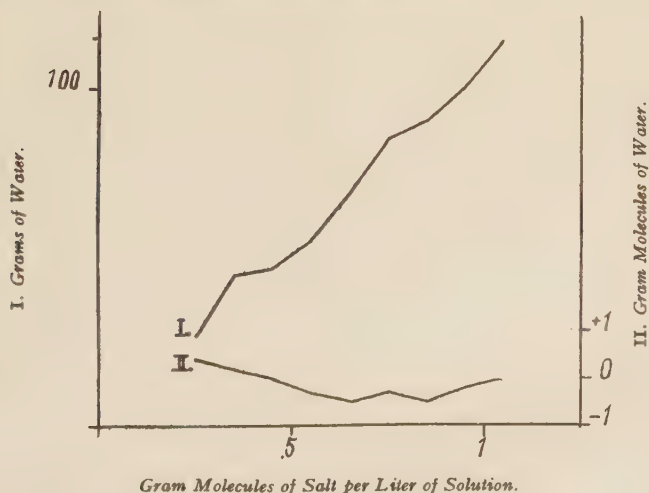


Fig. XI.

- I. Difference between the Amount of Water Present as Solvent in the Single Solution of Sodium Bromide and in the Mixture of Sodium Bromide and Lithium Bromide.
- II. Difference between the Values of M for Sodium Bromide in Single Solution and in the Mixture of Sodium Bromide and Lithium Bromide.

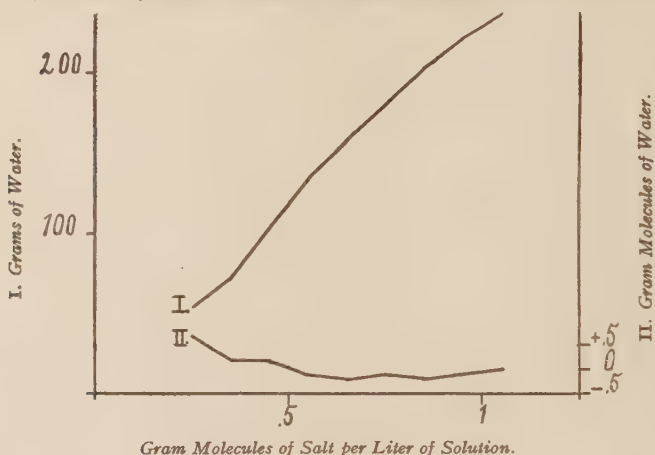


Fig. XII.

We next consider a mixture of calcium nitrate and magnesium nitrate, both of which have hydrating power.

CALCIUM NITRATE.

Table LXXIII.—Freezing Point Measurements.

m .	Δ .	Δ/m .	m .	Δ .	Δ/m .
0.25	1°.189	4.756	1.05	5°.123	4.88
0.45	2°.094	4.65	1.25	6°.345	5.08
0.65	3°.041	4.68	1.45	7°.547	5.21
0.85	4°.057	4.77	1.6555	8°.859	5.35

Table LXXIV.—Conductivity Measurements.

m .	V .	k .	Λv .	α .
0.25	4.0000	0.020975	83.9	0.624
0.45	2.2222	0.033259	73.9	0.550
0.65	1.5380	0.042932	66.0	0.491
0.85	1.1765	0.050272	59.2	0.440
1.15	0.9525	0.056301	53.6	0.399
1.25	0.8000	0.060363	48.3	0.359
1.45	0.6897	0.063236	43.6	0.324
1.6555	0.6041	0.064674	39.1	0.291

Table LXXV.—Weight-Normal Corrections.

<i>m.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.25	25.77665	1.0260	24.7405	1.0
0.45	26.3748	1.8467	24.5281	1.9
0.65	26.9693	2.6674	24.3019	2.8
0.85	27.5168	3.4882	24.2860	3.9
1.05	28.1060	4.3089	23.7971	4.8
1.25	28.6822	5.1297	23.5525	5.8
1.45	29.2340	5.9504	23.2836	6.9
1.6555	29.8480	6.7938	23.0542	7.8

Table LXXVI.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.25	0.624	4.18	4.76	4.71	6.3	25.2
0.45	0.550	3.90	4.65	4.56	8.0	17.9
0.65	0.491	3.69	4.68	4.55	10.5	16.2
0.85	0.440	3.50	4.77	4.58	13.1	15.4
1.05	0.391	3.34	4.88	4.65	15.7	15.0
1.25	0.359	3.20	5.08	4.79	18.4	14.7
1.45	0.324	3.07	5.21	4.85	20.4	14.1
1.6555	0.291	2.94	5.35	4.93	22.4	13.5

MAGNESIUM NITRATE.

Table LXXVII.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>m.</i>	Δ .	Δ/m .
0.25	1°.252	5.01	1.05	6°.762	6.44
0.45	2°.395	5.32	1.25	8°.562	6.85
0.65	3°.669	5.64	1.45	10°.589	7.30
0.85	5°.113	6.02			

Table LXXVIII.—Conductivity Measurements.

$$\Lambda_{\infty} 0^{\circ} = 128.5.$$

<i>m.</i>	<i>V.</i>	<i>k.</i>	Δv .	α .
0.25	4.0000	0.021563	86.3	0.671
0.45	2.2222	0.035123	78.1	0.607
0.65	0.5380	0.046942	72.2	0.562
0.85	1.1765	0.056821	66.9	0.520
1.05	0.9525	0.065334	62.2	0.484
1.25	0.8000	0.071668	57.3	0.446
1.45	0.68966	0.076279	52.6	0.409

Table LXXIX.—Weight-Normal Corrections.

<i>m.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.25	25.6880	0.9277	24.7603	1.0
0.45	26.2075	1.6699	24.5376	1.8
0.65	26.7605	2.4122	24.3483	2.6

Table LXXIX.—(Continued).

<i>m.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.85	27.1958	3.1543	24.0415	3.8
1.05	27.7080	3.8965	23.8115	4.8
1.25	28.2435	4.6287	23.6048	5.6
1.45	28.7626	5.3809	23.3817	6.5

Table LXXX.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	<i>Δ</i> / <i>m.</i>	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.25	0.671	4.36	5.01	4.96	6.7	26.8
0.45	0.607	4.12	5.32	5.22	11.7	26.0
0.65	0.562	3.95	5.64	5.49	15.6	24.0
0.85	0.520	3.80	6.02	5.79	19.1	22.5
1.05	0.484	3.66	6.44	6.13	22.4	21.3
1.25	0.446	3.52	6.85	6.47	25.3	20.2
1.45	0.409	3.38	7.30	6.83	28.1	19.4

Data for the *mixture* of calcium nitrate and magnesium nitrate follow:

Table LXXXI.—Freezing Point Measurements.

<i>m.</i>	<i>P.</i>	<i>Δ.</i>	<i>m.</i>	<i>P.</i>	<i>Δ.</i>
0.5 Ca(NO ₃) ₂	I	2° .498	2.1 Ca(NO ₃) ₂	I	19° .90
0.5 Mg(NO ₃) ₂	I		2.1 Mg(NO ₃) ₂	I	
0.9 Ca(NO ₃) ₂	I		2.5 Ca(NO ₃) ₂	I	
0.9 Mg(NO ₃) ₂	I	4° .856	2.5 Mg(NO ₃) ₂	I	19° .73
1.3 Ca(NO ₃) ₂	I		2°9 Ca(NO ₃) ₂	I	
1.3 Mg(NO ₃) ₂	I	7° .624	2.9 Mg(NO ₃) ₂	I	24° .8
1.7 Ca(NO ₃) ₂	I				
1.7 Mg(NO ₃) ₂	I	10° .93			

Table LXXXII.—Weight-Normal Corrections.

<i>m.</i>	<i>P.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.5 Ca(NO ₃) ₂	I	26.4387	1.9537	24.4850	2.1
0.5 Mg(NO ₃) ₂	I				
0.9 Ca(NO ₃) ₂	I				
0.9 Mg(NO ₃) ₂	I	27.5300	3.5166	24.0134	3.9
1.3 Ca(NO ₃) ₂	I				
1.3 Mg(NO ₃) ₂	I	28.5974	5.0796	23.5178	5.9
1.7 Ca(NO ₃) ₂	I				
1.7 Mg(NO ₃) ₂	I	29.6600	6.6425	23.0175	7.9
2.1 Ca(NO ₃) ₂	I				
2.1 Mg(NO ₃) ₂	I	30.6253	8.2055	22.4198	10.3
2.5 Ca(NO ₃) ₂	I				
2.5 Mg(NO ₃) ₂	I	31.6538	9.7684	21.8854	12.5
2.9 Ca(NO ₃) ₂	I				
2.9 Mg(NO ₃) ₂	I	32.6175	11.3313	21.2862	14.9

Table LXXXIII.—Conductivity Measurements.

m .	P .	m_c .	V_c .	k_u .	k .	D .	k_c .	Δv .	α .
0.5 Ca(NO ₃) ₂	1	0.25	4.0000	0.036833	0.020795	0.003705	0.019013	76.1	0.565
0.5 Mg(NO ₃) ₂	1	0.25	4.0000		0.021563		0.019820	79.3	0.671
0.9 Ca(NO ₃) ₂	1	0.45	2.2222	0.054700	0.033259	0.013682	0.025920	57.6	0.428
0.9 Mg(NO ₃) ₂	1	0.45	1.2222		0.035123		0.028780	64.0	0.498
1.3 Ca(NO ₃) ₂	1	0.65	1.538	0.065970	0.042932	0.023904	0.029904	46.0	0.342
1.3 Mg(NO ₃) ₂	1	0.65	1.538		0.046942		0.036066	55.5	0.432
1.7 Ca(NO ₃) ₂	1	0.85	1.1765	0.071201	0.050272	0.035892	0.030420	35.8	0.266
1.7 Mg(NO ₃) ₂	1	0.85	1.1765		0.056821		0.040781	48.0	0.373
2.1 Ca(NO ₃) ₂	1	1.05	0.9523	0.071673	0.056301	0.049962	0.028332	27.0	0.201
2.1 Mg(NO ₃) ₂	1	1.05	0.9523		0.065334		0.043341	41.3	0.321
2.5 Ca(NO ₃) ₂	1	1.25	0.8000	0.069140	0.060363	0.062891	0.024807	19.9	0.148
2.5 Mg(NO ₃) ₂	1	1.25	0.8000		0.071668		0.044433	35.5	0.276
2.9 Ca(NO ₃) ₂	1	1.45	0.68966	0.063327	0.063236	0.076188	0.019866	13.7	0.102
2.9 Mg(NO ₃) ₂	1	1.45	0.68966		0.076279		0.043461	30.0	0.233

Table LXXXIV.—Hydrates.

P equals 1 in each case.

<i>m.</i>	<i>m_c.</i>	<i>α.</i>	<i>L_c.</i>	<i>M.</i>	<i>Δ.</i>	Sp. Gr. Cor.	<i>H_c.</i>	<i>M_c.</i>
0.5 Ca(NO ₃) ₂	0.25	0.565	3.96	6.3	2.498	2.1	4.6	18.5
0.5 Mg(NO ₃) ₂	0.25	0.617	4.16	6.7			5.2	20.8
0.9 Ca(NO ₃) ₂	0.45	0.428	3.45	8.0	4.856	3.9	7.2	16.0
0.9 Mg(NO ₃) ₂	0.45	0.498	3.71	11.7			11.1	24.7
1.3 Ca(NO ₃) ₂	0.65	0.342	3.13	10.5	7.624	5.9	9.4	14.4
1.3 Mg(NO ₃) ₂	0.65	0.432	3.47	15.6			14.9	22.9
1.7 Ca(NO ₃) ₂	0.85	0.266	2.85	13.1	10.93	7.9	11.7	13.8
1.7 Mg(NO ₃) ₂	0.85	0.373	3.25	19.1			18.1	21.3
2.1 Ca(NO ₃) ₂	1.05	0.201	2.61	15.7	14.90	10.3	13.6	13.0
2.1 Mg(NO ₃) ₂	1.05	0.321	3.05	22.4			21.0	20.0
2.5 Ca(NO ₃) ₂	1.25	0.148	2.41	18.4	19.73	12.5	15.7	12.5
2.5 Mg(NO ₃) ₂	1.25	0.276	2.89	25.3			23.3	18.7
2.9 Ca(NO ₃) ₂	1.45	0.102	2.24	20.4	24.8	14.9	16.5	11.4
2.9 Mg(NO ₃) ₂	1.45	0.233	2.73	28.1			25.2	17.4

I. Magnesium Nitrate Alone.

II. Magnesium Nitrate Mixed with Calcium Nitrate.

III. Calcium Nitrate Alone.

IV. Calcium Nitrate Mixed with Magnesium Nitrate.

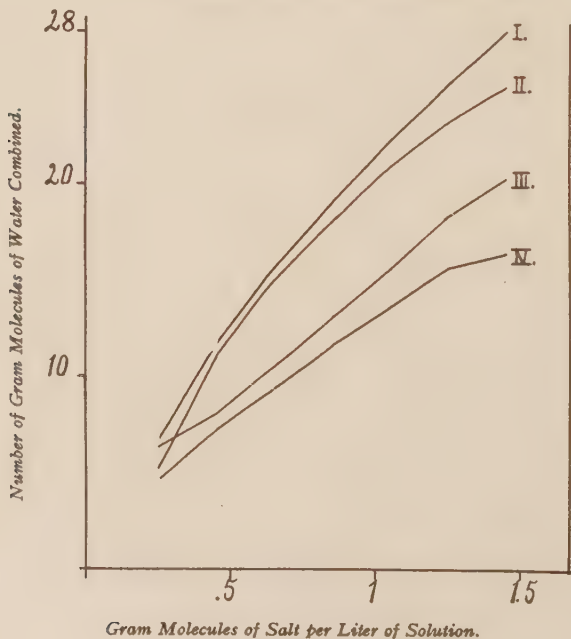


Fig. XIII.

The values of M for each salt in the mixture and in separate solution are plotted as curves in Fig. XIII. With increased concentration we have increased divergence in curves I. and III., which represent the hydrating power (values of M) in separate solutions of magnesium nitrate and of calcium nitrate, respectively. Consequently, as we should expect, curves II. and IV., representing the values of M for the two salts in the mixture, show increasing divergence with increase in concentration.

Table LXXXV.—Calcium Nitrate in Mixture of Calcium Nitrate and Magnesium Nitrate.

<i>m.</i>	D_{H_2O} .	D_m .	<i>m.</i>	D_{H_2O} .	D_m .
0.25	104.4	1.7	1.05	432.5	2.1
0.45	220.3	0.8	1.25	487.0	2.7
0.65	298.5	1.1	1.45	534.0	3.9
0.85	365.7	1.4			

Table LXXXVI.—Magnesium Nitrate in Mixture of Calcium Nitrate and Magnesium Nitrate.

<i>m.</i>	D_{H_2O} .	D_m .	<i>m.</i>	D_{H_2O} .	D_m .
0.25	93.7	1.5	1.05	300	1.4
0.45	150.5	0.6	1.25	351	2.0
0.65	202.0	0.7	1.45	381	2.9
0.85	251.0	1.0			

These values are plotted as curves in Figs. XIV. and XV.

The curves in Figs. XIV. and XV. show the same general relations as the preceding curves of the same character, excepting those of lithium bromide and sodium bromide. The amount of water eliminated to form hydrates in the mixture tends to diminish somewhat, proportionally to the diminution in the amount of water present which is acting as solvent. This is clearly shown by the direction in which the curves turn with increased concentration of the solutions. It is probable that in the more dilute solutions we have the difference in the hydrating power of the ions and molecules affecting the total amount of water eliminated as water of hydration. Consequently, where the total amount of salt is con-

stant, but a change in the dissociation is produced, if the number of ions is large relative to the number of molecules undissociated, as is the case in the more dilute solutions, the curve for D_m does not at once show the influence of diminishing the amount of solvent present. This phenomenon is shown by the curves as change of direction, or as increased curvature in the curve which represents the value of D_m .

A pair of quarternary electrolytes was next studied. Ferric chloride and calcium chloride were employed. Very concentrated stock solutions were prepared, and the necessary measurements were made as quickly as possible, in order to

- I. Difference between the Amount of Water Present as Solvent in the Single Solution of Calcium Nitrate and in the Mixture of Calcium Nitrate and Magnesium Nitrate.
- II. Difference between the Values of M for Calcium Nitrate in Single Solution and in the Mixture of Calcium Nitrate and Magnesium Nitrate.

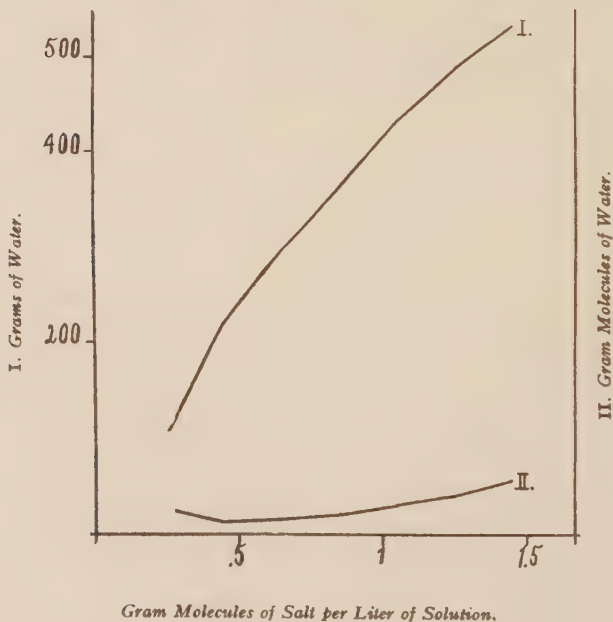
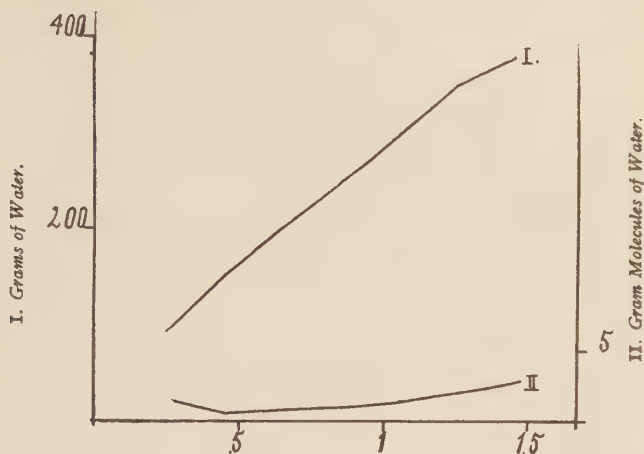


Fig. XIV.

- I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Magnesium Nitrate and in the Mixture of Magnesium Nitrate and Calcium Nitrate.*
- II. *Difference between the Values of M for Magnesium Nitrate in Single Solution and in the Mixture of Calcium Nitrate and Magnesium Nitrate.*



Gram Molecules of Salt per Liter of Solution.

Fig. XV.

reduce hydrolysis to a minimum, there being an appreciable time factor in the hydrolysis of such compounds as ferric chloride. Notwithstanding all precautions there was, of course, considerable hydrolysis. Especially was this the case in the mixture of the two salts, the presence of the aluminium chloride appearing to act catalytically upon the solution of ferric chloride, causing a gradual precipitation of ferric hydroxide.

ALUMINIUM CHLORIDE.

Table LXXXVII.—Freezing Point Measurements.

m .	Δ .	Δ/m .	m .	Δ .	Δ/m .
0.2	1°.279	6.40	1.0	11°.795	11.80
0.4	2°.910	7.28	1.2	16°.385	13.65
0.6	5°.144	8.57	1.3617	21°.75	15.97
0.8	7°.962	9.95	1.415	23°.50	16.60

Table LXXXVIII.—Conductivity Measurements.

$\Lambda_{\infty} 0^{\circ} = 181.7$ (Calculated from Jones and Getman's value of μ_{∞}).

<i>m.</i>	<i>V.</i>	<i>k.</i>	$\Delta v.$	$\alpha.$
0.2	5.000	0.023983	119.9	0.660
0.4	2.500	0.040530	101.3	0.558
0.6	1.6666	0.053115	88.5	0.487
0.8	1.250	0.061180	76.5	0.421
1.0	1.000	0.066595	66.6	0.367
1.2	0.8333	0.06842	57.0	0.314
1.3617	0.7344	0.06760	49.7	0.273

Table LXXXIX.—Weight-Normal Corrections.

<i>m.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.2	25.6240	0.6673	24.9567	0.2
0.4	26.1538	1.3346	24.8192	0.7
0.6	26.7134	2.0019	24.7115	1.2
0.8	27.2153	2.6692	24.5461	1.8
1.0	27.7351	3.3365	24.3986	2.4
1.2	28.2877	4.0038	24.2839	2.9
1.3617	28.7252	4.5433	24.1819	3.3

Table XC.—Hydrates.

<i>m.</i>	$\alpha.$	<i>L.</i>	$\Delta/m.$	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.2	0.660	5.54	6.40	6.39	7.4	37.0
0.4	0.558	4.97	7.28	7.23	7.4	43.5
0.6	0.487	4.58	8.57	8.47	25.5	42.5
0.8	0.421	4.21	9.95	9.77	31.6	39.5
1.0	0.367	3.91	11.80	11.52	36.7	36.7
1.2	0.314	3.61	13.65	13.25	40.4	33.7
1.3617	0.273	3.39	15.97	15.44	43.4	31.9

FERRIC CHLORIDE.

Table XCI.—Freezing Point Measurements.

<i>m.</i>	$\Delta.$	$\Delta/m.$	<i>m.</i>	$\Delta.$	$\Delta/m.$
0.2	1° 255	6.28	1.0	9° 152	9.15
0.4	2° 715	6.79	1.2	12° 11	10.09
0.6	4° 530	7.55	1.3617	14° 592	10.72
0.8	6° 667	8.33			

Table XCII.—Conductivity Measurements.

 $\Lambda_{\infty} 0^{\circ} = 220$ (calculated).

<i>m.</i>	<i>V.</i>	<i>k.</i>	$\Delta v.$	$\alpha.$
0.2	5.000	0.02380	119.0	0.541
0.4	2.500	0.03786	94.7	0.430
0.6	1.6666	0.04645	77.4	0.352
0.8	1.250	0.05147	64.3	0.292
1.0	1.000	0.053147	53.1	0.241
1.2	0.8333	0.053145	44.3	0.201
1.3617	0.7344	0.051777	38.0	0.173

Table XCIII.—Weight-Normal Corrections.

<i>m.</i>	<i>W_{Sol.}</i>	<i>W_{Salt.}</i>	<i>W_{H₂O.}</i>	Correction, per cent.
0.2	25.6792	0.8113	24.8679	0.5
0.4	26.3380	1.6225	24.7155	1.1
0.6	26.9956	2.4337	24.5619	1.8
0.8	27.6230	3.2450	24.3780	2.5
1.0	28.2400	4.056	24.1840	3.3
1.2	28.8867	4.8675	24.0192	3.9
1.3617	29.3690	5.5234	23.8456	4.6

Table XCIV.—Hydrates.

<i>m.</i>	$\alpha.$	<i>L.</i>	$\Delta/m.$	<i>L'.</i>	<i>M.</i>	<i>H.</i>
0.2	0.541	4.88	6.28	6.25	12.2	61.0
0.4	0.430	4.26	6.79	6.72	20.3	50.7
0.6	0.352	3.82	7.55	7.41	26.9	44.8
0.8	0.292	3.49	8.33	8.12	31.7	39.6
1.0	0.241	3.21	9.15	8.85	35.4	35.4
1.2	0.201	2.98	10.09	9.70	38.5	32.1
1.3617	0.173	2.82	10.72	10.23	40.2	29.5

MIXTURE OF FERRIC CHLORIDE AND ALUMINIUM CHLORIDE.

Table XCV.—Freezing Point Measurements.

<i>m.</i>	<i>P.</i>	$\Delta.$	<i>m.</i>	<i>P.</i>	$\Delta.$
0.4 FeCl ₃	I	2° .938	2.0 FeCl ₃	I	36° .0
0.4 AlCl ₃	I		2.0 AlCl ₃	I	
0.8 FeCl ₃	I	7° .28	2.4 FeCl ₃	I	56° .0
0.8 AlCl ₃	I		2.4 AlCl ₃	I	
1.2 FeCl ₃	I	13° .69	2.7234 FeCl ₃	I	84° .6
1.2 AlCl ₃	I		2.7234 AlCl ₃	I	
1.6 FeCl ₃	I	22° .5			
1.6 AlCl ₃	I				

It was necessary to extrapolate this last value, $84^{\circ}.6$, since the solution failed to freeze in the freezing mixture employed, *i. e.*, solid carbon dioxide and alcohol. The more concentrated solutions became so viscous, when cooled down, that it was difficult to stir them properly.

Table XCVI.—Weight-Normal Corrections.

<i>m.</i>	<i>P.</i>	<i>WSol.</i>	<i>WSalt.</i>	<i>WH₂O.</i>	Correction, per cent.
0.4 FeCl ₃	I	26.2807	1.4786	24.8021	0.8
0.4 AlCl ₃	I				
0.8 FeCl ₃	I	27.4365	2.9571	24.4794	2.1
0.8 AlCl ₃	I				
1.2 FeCl ₃	I	28.5660	4.4356	24.1304	3.5
1.2 AlCl ₃	I				
1.6 FeCl ₃	I	29.7105	5.9142	23.7963	4.8
1.6 AlCl ₃	I				
2.0 FeCl ₃	I	30.8182	7.3925	23.4257	6.3
2.0 AlCl ₃	I				
2.4 FeCl ₃	I	31.9182	8.8713	23.0469	7.8
2.4 AlCl ₃	I				
2.72 FeCl ₃	I	32.7777	10.0667	22.7110	9.2
2.72 AlCl ₃	I				

It is to be noted that the conductivity measurements which are given in the following table are the merest approximations to measurements of dissociation. The conductivity measurements are made at zero, whereas some of these mixtures freeze very considerably below 0° C. There is marked hydrolysis in some cases, as already mentioned, leading to a precipitation of the iron. There is considerable difference between the viscosity of the single solutions and of the mixtures where the normalities are the same. The assumption that these salts dissociate at once, in the most concentrated solutions, into $M^{+++} Cl^{-} Cl^{-} Cl^{-}$, is certainly not correct. Finally, the values of Λ_{∞} are obtained by calculation, and may differ considerably from the true values because of the factors just mentioned.

Table XCVII.—Conductivity Measurements.

$m.$	$P.$	$m_c.$	$V_c.$	$k_u.$	$k.$	$D.$	$k_c.$	$\Lambda_v.$	$\alpha.$
0.4 FeCl ₃	I	0.2	5.000	0.040318	0.02380	0.007465	0.01935	96.8	0.440
0.4 AlCl ₃	I	0.2	5.000		0.023983		0.020968	104.8	0.577
0.8 FeCl ₃	I	0.4	2.500		0.03786		0.026928	67.3	0.306
0.8 AlCl ₃	I	0.4	2.500	0.060462	0.04053	0.017928	0.033534	83.7	0.461
1.2 FeCl ₃	I	0.6	1.6666		0.04645		0.019059	31.8	0.144
1.2 AlCl ₃	I	0.6	1.6666	0.055874	0.053115	0.043691	0.036815	61.4	0.338
1.6 FeCl ₃	I	0.8	1.250		0.05147		0.016040	20.1	0.091
1.6 AlCl ₃	I	0.8	1.250	0.056904	0.06118	0.055750	0.040860	51.1	0.281
2.0 FeCl ₃	I	1.0	1.00		0.053147		0.006597	6.6	0.030
2.0 AlCl ₃	I	1.0	1.00	0.047916	0.066595	0.071826	0.041319	41.3	0.227
2.4 FeCl ₃	I	1.2	0.8333		0.053145		0.00000	00.0	0.000
2.4 AlCl ₃	I	1.2	0.8333	0.037866	0.06842	0.083699	0.03787	31.6	0.174
2.72 FeCl ₃	I	1.3617	0.7344		0.051777		0.00000	00.0	0.000
2.72 AlCl ₃	I	1.3617	0.7344	0.029595	0.06760	0.089782	0.029595	21.7	0.120

Table XCVIII.—Hydrates.

P equals 1 in each case.

<i>m.</i>	<i>m_c.</i>	<i>α.</i>	<i>L_c.</i>	<i>M.</i>	<i>Δ.</i>	Sp. Gr. Cor.	<i>M_c.</i>	<i>H_c.</i>
0.4 FeCl ₃	0.2	0.440	4.31	12.2	2.938	0.8	13.5	67.5
0.4 AlCl ₃	0.2	0.577	5.08	7.4			8.2	41.0
0.8 FeCl ₃	0.4	0.306	3.57	20.3	7.288	2.1	19.6	49.0
0.8 AlCl ₃	0.4	0.461	4.44	17.4			16.6	41.5
1.2 FeCl ₃	0.6	0.144	2.67	26.9	13.69	3.5	25.8	43.0
1.2 AlCl ₃	0.6	0.338	3.74	25.5			24.4	40.7
1.6 FeCl ₃	0.8	0.091	2.37	31.7	22.5	4.8	29.0	36.2
1.6 AlCl ₃	0.8	0.281	3.43	31.6			28.9	36.1
2.0 FeCl ₃	1.0	0.030	2.03	35.4	36.0	6.3	32.2	32.2
2.0 AlCl ₃	1.0	0.227	3.02	36.7			33.7	33.7
2.4 FeCl ₃	1.2	0.000	1.86	38.5	56.0	7.8	34.6	28.8
2.4 AlCl ₃	1.2	0.174	2.83	40.4			36.7	30.6
2.7234 FeCl ₃	1.3617	0.000	1.86	40.2	84.6	9.2	36.1	26.5
2.7234 AlCl ₃	1.3617	0.120	2.53	43.4			39.6	29.0

These values of *M* and of *M_c* are plotted as curves in Fig. XVI. The general relation shown by these curves are the same as have previously been pointed out. The fact that the hydrating power of both the aluminium chloride and the ferric chloride is apparently greater in the mixture than in the separate solutions, in the most dilute solutions employed, is probably due to the effect of hydrolysis in increasing the value of *L*, and consequently diminishing *M*, though it may possibly be due, in part, to change in dissociation and difference in the hydrating power of the ions and molecules. It should be noted, also, that the hydrating power of the aluminium chloride appears to be relatively less than that of the ferric chloride in the more dilute solutions, but that this relation is reversed in the more concentrated solutions. This may be due to hydrolysis, since, if the aluminium chloride hydrolyzes more rapidly than the ferric chloride, then, in the more dilute solutions, where the effects of hydrolysis would be pronounced, the result would be to increase the value of *L* and, consequently, to diminish the value of *M*, based upon it.

- I. Aluminium Chloride Alone.
 II. Aluminium Chloride Mixed with Ferric Chloride.
 III. Ferric Chloride Alone.
 IV. Ferric Chloride Mixed with Aluminium Chloride.

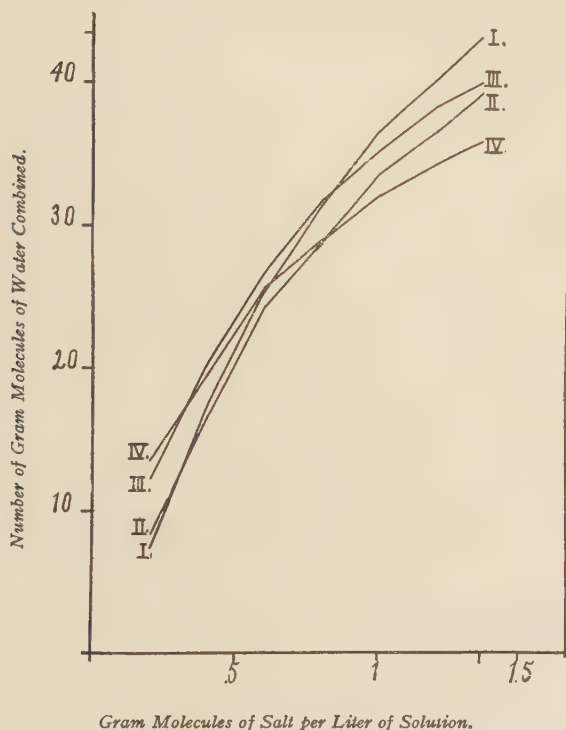


Fig. XVI.

In Tables XCIX. and C. the abbreviations have the usual significance.

Table XCIX.—Aluminium Chloride in Mixture of Aluminium Chloride and Ferric Chloride.

<i>m.</i>	<i>DH₂O.</i>	<i>D_{m.}</i>	<i>m.</i>	<i>DH₂O.</i>	<i>D_{m.}</i>
0.2	367	—0.8	1.0	618	3.0
0.4	249	0.8	1.2	671	3.7
0.6	488	1.1	1.3617	709	3.8
0.8	552	2.7			

Table C.—*Ferric Chloride in Mixture of Aluminium Chloride and Ferric Chloride.*

<i>m.</i>	D_{H_2O} .	D_m .	<i>m.</i>	D_{H_2O} .	D_m .
0.2	150	—1.3	1.0	636	3.2
0.4	308	0.7	1.2	699	3.9
0.6	456	1.1	1.3617	758	4.1
0.8	543	2.7			

These values are plotted as curves in Figs. XVII. and XVIII.

The effect of decrease in the amount of water present as solvent is plainly shown in the diminishing values of M as the amount of solvent is lessened. The slight irregularities are probably due to unavoidable experimental error, and inaccuracy of the conductivity method as a measure of dissociation.

- I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Aluminium Chloride and in the Mixture of Ferric Chloride and Aluminium Chloride.*
- II. *Difference between the Values of M for Aluminium Chloride in Single Solution and in the Mixture of Aluminium Chloride and Ferric Chloride.*

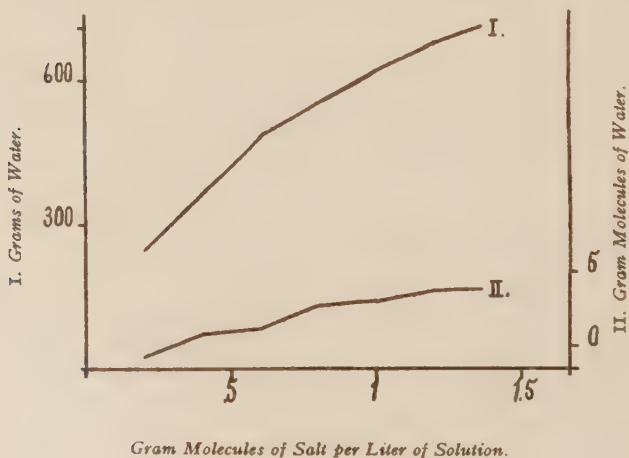
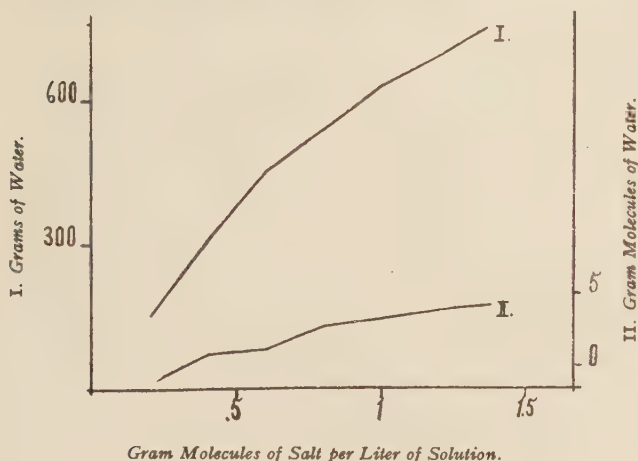


Fig. XVII.

- I. Difference between the Amount of Water Present as Solvent in the Single Solution of Ferric Chloride and in the Mixture of Ferric Chloride and Aluminium Chloride.
- II. Difference between the Values of M for Ferric Chloride in Single Solution and in the Mixture of Ferric Chloride and Aluminium Chloride.



XVIII.

Thus far all of the salts studied have a common anion. In order to extend the investigation to a pair of salts having a common cation, a mixture of calcium nitrate and calcium chloride was employed.

The data for the separate solutions of these two salts has already been given. The results obtained with the mixture follow:

Table CI.—Freezing Point Measurements.

$m.$	$P.$	$\Delta.$	$m.$	$P.$	$\Delta.$
0.5 $\text{Ca}(\text{NO}_3)_2$	I	$2^\circ.50$	2.1 $\text{Ca}(\text{NO}_3)_2$	I	$14^\circ.78$
0.5 CaCl_2	I		2.1 CaCl_2	I	
0.9 $\text{Ca}(\text{NO}_3)_2$	I	$4^\circ.88$	2.5 $\text{Ca}(\text{NO}_3)_2$	I	$19^\circ.2$
0.9 CaCl_2	I		2.5 CaCl_2	I	
1.3 $\text{Ca}(\text{NO}_3)_2$	I	$7^\circ.67$	2.9 $\text{Ca}(\text{NO}_3)_2$	I	$24^\circ.2$
1.3 CaCl_2	I		2.9 CaCl_2	I	
1.7 $\text{Ca}(\text{NO}_3)_2$	I	$11^\circ.00$	3.31102 $\text{Ca}(\text{NO}_3)_2$	I	$30^\circ.7$
1.7 CaCl_2	I		3.31102 CaCl_2	I	

Table CII.—Conductivity Measurements.

<i>m.</i>	<i>P.</i>	<i>m_c.</i>	<i>V_c.</i>	<i>k_u.</i>	<i>k.</i>	<i>D.</i>	<i>k_c.</i>	$\Delta v.$	$\alpha.$
0.5 Ca(NO ₃) ₂	I	0.25	4.0000	0.039475	0.020975	0.055730	0.018254	73.0	0.543
0.5 CaCl ₂	I	0.25	4.0000		0.024073		0.021221	84.9	0.575
0.9 Ca(NO ₃) ₂	I	0.45	2.2222		0.032590		0.026780	59.5	0.442
0.9 CaCl ₂	I	0.45	2.2222	0.059937	0.039688	0.013010	0.033157	73.7	0.499
1.3 Ca(NO ₃) ₂	I	0.65	1.5380		0.042632		0.030833	47.4	0.353
1.3 CaCl ₂	I	0.65	1.5380	0.073550	0.054236	0.023618	0.042716	65.7	0.445
1.7 Ca(NO ₃) ₂	I	0.85	1.1765		0.050272		0.031691	37.3	0.277
1.7 CaCl ₂	I	0.85	1.1765	0.081797	0.066903	0.035378	0.050106	59.0	0.400
2.1 Ca(NO ₃) ₂	I	1.05	0.9523		0.056301		0.029266	27.9	0.207
2.1 CaCl ₂	I	1.05	0.9523	0.084100	0.078344	0.050445	0.054834	52.2	0.354
2.5 Ca(NO ₃) ₂	I	1.25	0.8000		0.060363		0.023751	19.0	0.141
2.5 CaCl ₂	I	1.25	0.8000	0.068281	0.088853	0.066535	0.058930	47.1	0.320
2.9 Ca(NO ₃) ₂	I	1.45	0.68966		0.063236		0.016375	11.3	0.084
2.9 CaCl ₂	I	1.45	0.68966	0.077154	0.097385	0.083467	0.060780	41.9	0.284
3.311 Ca(NO ₃) ₂	I	1.6555	0.60405		0.064674		0.008650	5.2	0.039
3.311 CaCl ₂	I	1.6555	0.60405	0.069853	0.003300	0.098121	0.061203	37.0	0.251

Table CIII.—Weight-Normal Corrections.

<i>m.</i>	<i>P.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction, per cent.
0.5 Ca(NO ₃) ₂	I	26.3336	1.7197	24.6139	1.5
0.5 CaCl ₂	I				
0.9 Ca(NO ₃) ₂	I	27.3415	3.0954	24.2461	3.0
0.9 CaCl ₂	I				
1.3 Ca(NO ₃) ₂	I	28.3615	4.4711	23.8904	4.4
1.3 CaCl ₂	I				
1.7 Ca(NO ₃) ₂	I	29.3082	5.8469	23.4613	6.2
1.7 CaCl ₂	I				
2.1 Ca(NO ₃) ₂	I	30.2933	7.3260	23.0707	7.7
2.1 CaCl ₂	I				
2.5 Ca(NO ₃) ₂	I	31.2197	8.5984	22.6213	9.5
2.5 CaCl ₂	I				
2.9 Ca(NO ₃) ₂	I	32.1762	9.9741	22.2021	11.2
2.9 CaCl ₂	I				
3.311 Ca(NO ₃) ₂	I	33.0792	11.3878	21.6914	13.2
3.311 CaCl ₂	I				

Table CIV.—Hydrates.

P equals 1 in each case.

<i>m.</i>	<i>m_c.</i>	<i>α.</i>	<i>L_c.</i>	<i>M.</i>	<i>Δ.</i>	Sp. Gr. Cor.	<i>M_c.</i>	<i>H_c.</i>
Ca(NO ₃) ₂	0.25	0.543	3.88	6.3	2.50	1.5	4.6	18.4
CaCl ₂	0.25	0.575	4.00	8.2			7.0	28.0
Ca(NO ₃) ₂	0.45	0.442	3.51	8.0	4.88	3.0	7.4	16.4
CaCl ₂	0.45	0.499	3.72	11.7			11.2	24.9
Ca(NO ₃) ₂	0.65	0.353	3.17	10.5	7.67	4.4	9.5	14.8
CaCl ₂	0.65	0.445	3.52	15.7			15.1	23.2
Ca(NO ₃) ₂	0.85	0.277	2.89	13.1	11.00	6.2	12.1	14.2
CaCl ₂	0.85	0.400	3.35	18.9			18.2	21.4
Ca(NO ₃) ₂	1.05	0.207	2.63	15.7	14.78	7.7	14.1	13.4
CaCl ₂	1.05	0.354	3.18	21.9			20.8	19.8
Ca(NO ₃) ₂	1.25	0.141	2.39	18.4	19.20	9.5	16.4	13.1
CaCl ₂	1.25	0.320	3.05	24.3			22.8	18.2
Ca(NO ₃) ₂	1.45	0.084	2.17	20.4	24.2	11.2	17.6	12.1
CaCl ₂	1.45	0.284	2.92	27.3			25.2	17.4
11 Ca(NO ₃) ₂	1.6555	0.039	2.01	22.4	30.7	13.2	16.4	9.9
11 CaCl ₂	1.6555	0.251	2.79	30.1			25.6	15.5

The above values of *M* are plotted as curves in Fig. XIX. The results are of the same character as those shown by the preceding mixtures. The most concentrated solution measured shows a somewhat lower value for *M* in the mixture than we should expect, but it must be borne in mind that at

this great concentration the experimental errors involved are necessarily very large.

- I. Calcium Chloride Alone.
- II. Calcium Chloride Mixed with Calcium Nitrate.
- III. Calcium Nitrate Alone.
- IV. Calcium Nitrate Mixed with Calcium Chloride.

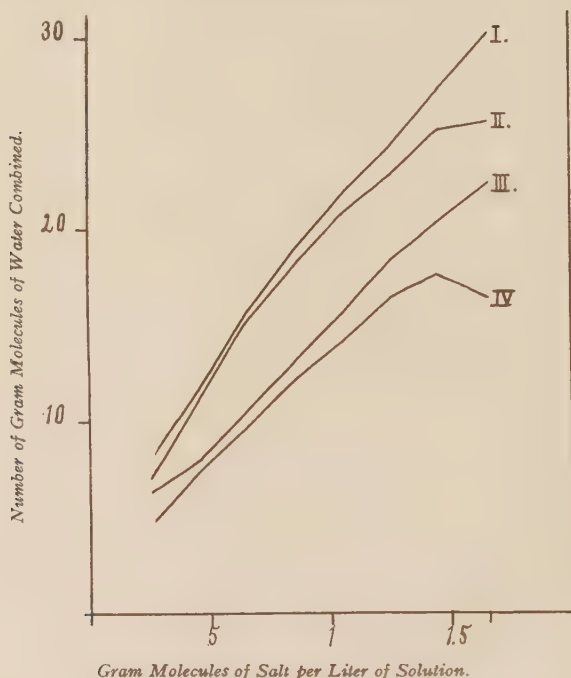


Fig. XIX.

Tables CV. and CVI. contain the data necessary to compare the change in the amount of solvent present with the change in the values of M in separate solution and in the mixture.

Table CV.—Calcium Chloride in Mixture of Calcium Nitrate and Calcium Chloride.

m .	DH_2O .	D_m .	m .	DH_2O .	D_m .
0.25	92	1.2	1.05	306	1.1
0.45	153	0.5	1.25	358	1.5
0.65	202	0.6	1.45	392	2.1
0.85	260	0.7	0.65555	386	4.5

Table CVI.—Calcium Nitrate in Mixture of Calcium Nitrate and Calcium Chloride.

<i>m.</i>	D_{H_2O}	D_m	<i>m.</i>	D_{H_2O}	D_m
0.25	131	1.7	1.05	404	1.6
0.45	213	0.6	1.25	447	2.0
0.65	288	0.9	1.45	496	2.8
0.85	350	1.0	1.6555	575	6.0

These values are plotted as curves in Figs. XX. and XXI. A diminution in the amount of water present as solvent causes a diminution in the value of M . This effect appears to be greater with increasing concentration. It is probable that in the most dilute solutions the difference in the hydrating power of the ions and molecules affects the curve, changing its direction.

- I. Difference between the Amount of Water acting as Solvent toward the Calcium Nitrate in the Mixture of Calcium Nitrate and Calcium Chloride and in the Separate Solution of Calcium Nitrate.
- II. Difference between the Values of M for Calcium Nitrate in Separate Solution and in the Mixture of Calcium Nitrate and Calcium Chloride.

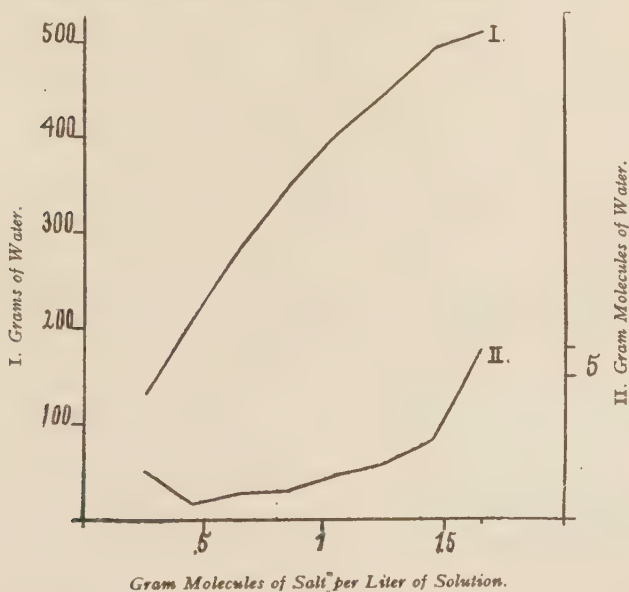


Fig. XX.

- I. Difference between the Amount of Water acting as Solvent toward the Calcium Chloride in the Mixture of Calcium Nitrate and Calcium Chloride and in the Separate Solution of Calcium Chloride.
- II. Difference between the Values of M for Calcium Chloride in Separate Solution and in the Mixture of Calcium Nitrate and Calcium Chloride.

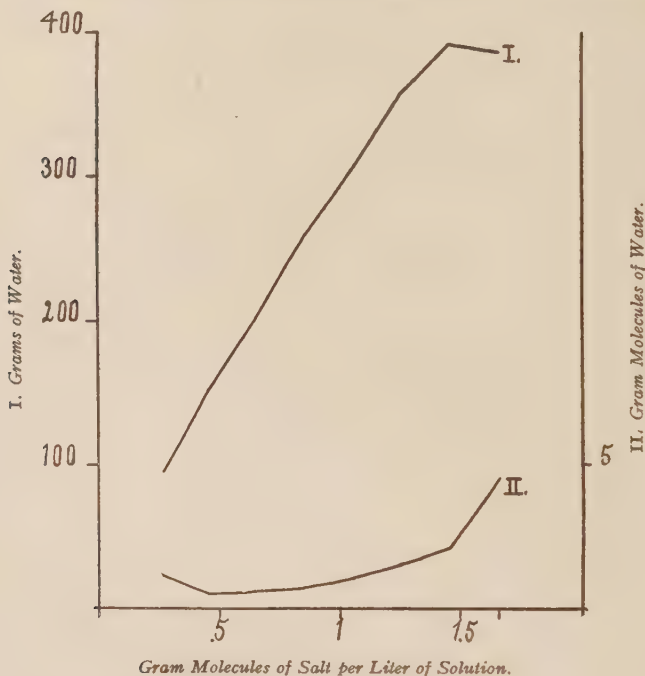


Fig. XXI.

THE EFFECT OF CHANGE IN TEMPERATURE ON THE CONDUCTIVITIES OF SEPARATE SOLUTIONS OF ELECTROLYTES AND ON MIXTURES OF THESE ELECTROLYTES.

In this paper we have repeatedly called attention to the fact that the conductivity method furnishes us with only an approximate value of the dissociation of a salt. The conductivity method of measuring dissociation is, however, the most general one available. In order to study the effect of change of temperature upon the conductivities of separate solutions of electrolytes and upon mixtures of these electrolytes, it was necessary to select a pair of salts which do not

form double salts in solution and which have little or no hydrating power. Potassium chloride and ammonium chloride were used.

The conductivities of single solutions of these salts and of their mixture were studied at 0° and 12°. Comparisons having shown that our values agree very closely with those obtained by Jones and West¹ and by Jones and Knight,² the values of Jones and Knight, at 25°, were used. The values of Jones and West, at 18°, show a very close agreement with those obtained experimentally by Kohlrausch at the same temperature. The values for potassium chloride at 25° are taken from the results of Kohlrausch.

POTASSIUM CHLORIDE.

Table CVII.—Molecular Conductivities.

<i>V.</i>	$\mu_{0^{\circ}}$	$\mu_{12^{\circ}}$	<i>V.</i>	$\mu_{25^{\circ}}$
1	61.58	82.05	1	104.1
2	63.02	84.43	2	108.6
5	65.85	87.84	4	111.2
20	68.59	92.88	16	121.5
100	72.13	98.69	80	128.5
200	73.73	101.3	160	131.1
1000	74.31	103.3	640	133.9

AMMONIUM CHLORIDE.

Table CVIII.—Molecular Conductivities.

<i>V.</i>	$\mu_{0^{\circ}}$	$\mu_{12^{\circ}}$	<i>V.</i>	$\mu_{25^{\circ}}$
1	61.08	81.15	1	99.3
2	62.53	83.57	2	104.9
5	63.98	87.66	4	110.4
20	68.13	93.19	16	120.9
100	71.64	99.94	80	131.8
200	72.89	101.3	160	134.2
1000	74.10	103.7	640	138.1

Since we are employing some of the values of Jones and West, Jones and Knight, and Kohlrausch, at 25°, we have tabulated a few values taken from these sources side by side with our own.

¹ THIS JOURNAL, 34, 381 (1905).

² *Ibid.*, 22, 125 (1899).

POTASSIUM CHLORIDE.

Table CIX.—Comparison of Conductivities.

V.	Jones and Stine.	Jones and West.	Jones and West.	Kohlrausch.
	$\mu_v 0^\circ$.	$\mu_v 0^\circ$.	$\mu_v 18^\circ$.	$\mu_v 18^\circ$.
1	61.58	...	...	...
2	63.02	62.96	95.9	95.8
5	65.85	...	...	...
8	...	66.47	103.6	...
16	...	68.40	107.0	...
20	68.59	...	...	108.3
32	...	70.27	110.7	...
120	72.13	...	...	114.7
128	...	73.00	115.5	...
200	73.73	...	...	...
1000	74.31	...	...	119.3
1024	...	75.14	119.3	...

AMMONIUM CHLORIDE.

Table CX.—Comparison of Conductivities.

V.	Jones and Stine.	Jones and West.	Jones and West.	Kohlrausch.
	$\mu_v 0^\circ$.	$\mu_v 0^\circ$.	$\mu_v 18^\circ$.	$\mu_v 18^\circ$.
1	61.08	...	...	...
2	62.53	62.76	96.3	94.8
5	63.98	...	...	...
8	...	66.17	103.6	...
16	...	68.02	107.2	...
20	68.13	...	...	107.8
32	...	70.2	110.8	...
100	71.64	...	...	114.2
128	...	73.08	...	...
200	72.89	...	116.2	...
1000	74.10	...	...	119.0
1024	...	74.84	119.6	...

Table CXI.—Comparison of Conductivities.

Jones and West.		Jones and Knight.	
V.	$\mu_v 25^\circ$	V.	$\mu_v 25^\circ$
1	...	160	134.2
2	109.2	512	136.8
8	118.6	640	138.1
16	123.2	1024	...
32	127.6	1600	138.9
128	133.4	...	...

In connection with the conductivity of ammonium chloride, Jones and Knight say:¹ "The values which we found for the conductivity of ammonium chloride differed slightly from those obtained by Kohlrausch,² our values being somewhat lower in the more concentrated solutions, as a little higher in the more dilute. This difference is probably due to the temperature coefficient which must be added to Kohlrausch's values, to transform them from 18° to 25°." This coefficient was uncertain over any considerable range of temperature.

POTASSIUM CHLORIDE.

Table CXII.—Comparison of Conductivities.

<i>V.</i>	Jones and West. μv 25°.	Jones and Knight. (Kohlrausch). μv 25°.	<i>V.</i>	Jones and West. μv 25°.	Jones and Knight. (Kohlrausch). μv 25°.
1	...	104.5	160	...	131.1
2	109.5	108.6	512	135.5	...
8	118.6	116.5	640	...	133.9
16	122.9	121.5	1024	137.0	...
32	126.8	125.4	1600	...	135.4
128	132.4	...			

From these tables it is evident that our values agree very well with those of Kohlrausch, Jones and West, and Jones and Knight.

Let us turn, now, to the conductivities of the mixtures of potassium chloride and ammonium chloride. These solutions were mixed in equal volumes. When, for example, a 2.0 N solution of potassium chloride is added to an equal volume of 2.0 N ammonium chloride, the assumption that the resulting solution consists of 1.0 N potassium chloride and 1.0 N ammonium chloride is evidently not quite correct, because of the volume occupied by the salt in the added solution. In order to make the necessary correction for this factor, pycnometer measurements were made with the more concentrated solutions. In the more dilute solutions this factor is so small that it is entirely negligible.

¹ THIS JOURNAL, 22, 117 (1899).

² Wied. Ann., 26, 161.

In the following table, m is the normality; C is the capacity of the pycnometer in cubic centimeters; W_{Salt} is the weight of salt present in the solution; W_{H_2O} is the weight of water present in the volume of solution contained in the pycnometer; and v is the volume of water in a thousand cubic centimeters of the solution.

Table CXIII.—Potassium Chloride, at 12° .

m .	C .	W_{Salt} .	W_{H_2O} .	V .
0.05	24.4259	0.0911	24.3821	998.66
0.20	23.9474	0.35373	23.8077	994.62
0.50	11.6945	0.4362	11.5294	986.35
1.00	12.6976	0.9472	12.3370	972.16

Table CXIV.—Ammonium Chloride, at 12° .

m .	C .	W_{Salt} .	W_{H_2O} .	V .
0.2	24.3605	0.2608	24.1679	992.54
0.4	24.4259	0.5229	24.0573	985.37
0.6	23.9474	0.7690	23.4098	978.00
0.8	12.6976	0.5437	12.3176	970.52
1.0	11.6945	0.6259	11.2574	963.07

Based upon these measurements, the conductivity of the potassium chloride and ammonium chloride in the various mixtures was calculated, on the assumption that no change in the dissociation of these salts takes place when their solutions are mixed. The results are given, along with the conductivities of the mixtures, in the following tables:

Table CXV.—Comparison for Potassium Chloride, Ammonium Chloride.

V .	KCl μv 25° .	V .	NH ₄ Cl μv 25° .	Sum.	KCl + NH ₄ Cl V , μv 25° .	Difference.
1	104.1	1	99.3	203.4	1 179.3	24.1
2	108.6	2	104.9	213.5	2 195.0	18.5
4	111.2	4	110.4	221.6	4 208.3	13.3
8	116.5	8	115.8	232.3	8 220.9	11.4
16	121.5	16	120.9	242.4	16 231.7	10.7
32	125.4	32	125.3	250.7	32 241.2	9.5
40	125.7	40	127.6	253.3	40 245.9	7.4
80	128.5	80	131.8	260.3	80 254.3	6.0
160	131.1	160	134.2	265.3	160 263.3	3.0
320	132.1	320	136.8	268.9	320 267.0	1.9
640	133.9	640	138.1	272.0	640 273.1	—1.1
1600	135.4	1600	138.9	274.3	1600 279.1	—4.8

Table CXVI.—Comparison for Potassium Chloride, Ammonium Chloride.

(Jones and Knight).							
<i>V.</i>	KCl μ_v 12°.	<i>V.</i>	NH ₄ Cl μ_v 12°.	Sum.	<i>V.</i>	KCl + NH ₄ Cl μ_v 12°.	Difference.
1	81.95	1	81.10	163.1	1	154.9	8.2
2	84.38	2	83.55	167.9	2	161.1	6.8
5	87.82	5	87.66	175.5	5	170.5	5.0
20	92.88	20	93.19	186.1	20	181.3	4.8
100	98.69	100	99.94	198.6	100	194.7	3.9
200	101.3	200	101.3	202.6	200	199.7	2.9
1000	103.3	1000	103.7	207.0	1000	208.7	—1.7

Table CXVII.—Comparison for Potassium Chloride, Ammonium Chloride.

V.	KCl μ_v 0°.	V.	NH ₄ Cl μ_v 0°.	Sum.	V.	KCl + NH ₄ Cl μ_v 0°.	Difference.
1	61.48	1	61.03	122.5	1	121.2	1.3
2	62.97	2	62.51	125.5	2	122.8	2.7
5	65.83	5	63.97	129.8	5	126.9	2.9
20	68.59	20	68.13	136.7	20	133.4	3.3
100	72.13	100	71.64	143.6	100	141.2	2.6
200	73.73	200	72.89	146.6	200	144.9	1.7
1000	74.31	1000	74.10	148.4	1000	147.5	0.9

Table CXVIII.—Comparison of Differences.

V.	Diff. 0°.	Diff. 12°.	Diff. 25°.
1	1.3	8.2	24.1
2	2.7	6.8	18.5
5	2.9	5.0	12.8
20	3.3	4.8	10.4
100	2.6	3.9	5.2
200	1.7	2.9	2.7
1000	0.9	—1.7	—2.5

If this change in the conductivity, when the solutions are mixed, is due only to a suppression of ionization, then we should expect the suppression to be nearly the same at the various temperatures, since the dissociation is very nearly the same at these various temperatures (*vide* Tables CXIX., CXX.).

Table CXIX.—Dissociation of Potassium Chloride.

<i>V.</i>	α 0°.	α 12°.	α 25°.
1	0.827	0.793	0.768
2	0.847	0.817	0.802
5	0.886	0.850	0.831
20	0.923	0.899	0.905
100	0.971	0.955	0.954
200	0.992	0.981	0.970
1000	1.00	1.00	0.993

Table CXX.—Dissociation of Ammonium Chloride.

<i>V.</i>	α 0°.	α 12°.	α 25°.
1	0.824	0.782	0.715
2	0.844	0.806	0.755
5	0.863	0.845	0.805
20	0.919	0.899	0.878
100	0.967	0.964	0.953
200	0.984	0.977	0.970
1000	1.00	1.00	0.997

If the suppression of the ionization is the only cause of the diminution in the conductivity when the solutions are mixed, then the greatest diminution should take place where the more highly dissociated salts are mixed; that is, the diminution in conductivity should be slightly greater at 0° than at 12°, and slightly greater at 12° than at 25°. Just the opposite is shown to be true by Table CXVIII. Again, if this lessening of conductivity is dependent upon the amount of dissociation alone, then, since the difference between the dissociation at 0° and 12° is the same or a little greater than the difference between the dissociation at 12° and 25° (save in some cases in the ammonium chloride), we should expect to find the difference between the columns headed Diff. 12° and Diff. 0°; in Table CXVIII., the same or slightly greater than the difference between the columns headed Diff. 12° and Diff. 25°. The opposite is true—the difference between columns 2 and 3 being from two to four times as great as that between 1 and 2, up to $V = 100$. At $V = 100$ the differences are the same, and at $V = 200$ and $V = 1000$ the columns headed Diff. 25° becomes smaller than the other two.

We must, then, look elsewhere for the cause of at least a part of the change in the conductivities, since it is evidently not due *solely* to change in dissociation, especially since some of the solutions mixed are nearly isohydric. There are three other factors which might come into play: Change in hydration, giving rise to a change in the dimensions of the ionic sphere; change in the viscosity of the solution with change in temperature; change in the number of the dissolved particles (ions and molecules). Of these three possibilities the first probably does not affect the conductivity appreciably, there being little hydration in these cases. The second is probably the principal factor in causing changes in the conductivity with changes in temperature. The third—change in the number of the dissolved particles—may also play some part, since the value of α becomes smaller with rise in temperature, and, other things being equal, the fewer the number of ions and molecules with which a moving ion must collide, the less the friction it will encounter. The differences in the values of columns 1, 2, and 3 are greatest for the most concentrated solutions, and it is in these solutions that the greatest change in the value α , with rise in temperature, is noted.

Clearly, values for α which are based upon the conductivity of the completely dissociated molecules at high dilution cannot be correct, since the conductivity of this completely dissociated solution must be considerably altered by change in viscosity and in the number of dissolved ions or molecules, both of which factors enter on increasing the concentration, the number of ions and molecules present undergoing especially great alteration.

SUMMARY.

It has been shown:

1. That the complexity of the hydrates formed by a salt is a function of the amount of water present as solvent.
2. That when two salts are present in the same solution, the complexity of the hydrates is somewhat less than in separate solutions of these salts, each salt tending to dehydrate the other.

3. That the ions and the molecules of salts probably have different hydrating power.

4. That the hydrating power of the molecules is in some cases probably greater than that of the ions into which these molecules dissociate.

5. Additional proof is furnished for the view that the conductivity method is by no means an accurate measure of dissociation.

6. It has been pointed out that the diminution in conductivity which takes place when two electrolytes of the type potassium chloride, ammonium chloride are mixed is probably not due entirely to suppression of ionization, but also to

A. Change in the viscosity of the solvent;

B. Change in the size of the ionic sphere, due to alteration in the amount of water which the ion must drag with it through the solution.

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May, 1907.

BIOGRAPHY.

Charles M. A. Stine was born in Norwich, Connecticut, on October 18, 1882. His preparatory training was received in public schools and academies, in various states. He entered Pennsylvania College in 1897, where he received the degree A. B. in 1901. In 1902 he returned to Pennsylvania College for special work in Chemistry, receiving the degree of B. S. in 1903, that of A. M. in 1904 and that of M. S. in 1906. During the two years preceding his enrolment in the Johns Hopkins University he taught Chemistry and Mathematics in Maryland College.

In October, 1905, he entered the Johns Hopkins University as a graduate student in Chemistry, with Physical Chemistry and Mineralogy as subordinate subjects. The most of his time was devoted to Physical Chemistry, and his dissertation was prepared in this field. In 1906-1907 he held a Fellowship in Chemistry at the University.

